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PAPERS ACCEPTED FOR PUBLICATION:

Action of Hydrochloric Acid Gas upon the Salts of the Elements of Group V of the Periodic System. By Edgar F. Smith and Jos. H. Hibbs.

Sketch of Lothar Meyer. By J. H. Long.

Issued with July Number. 1895.

Proceedings.

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An invitation from Cleveland, Ohio, to hold the winter meeting at that place has been accepted by Council.

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MEETINGS OF THE SECTIONS.

LEHIGH VALLEY SECTION.

The regular monthly meeting was held at Lehigh University, South Bethlehem, on the evening of May 2. There were fourteen present. Porter W. Shimer read a paper on the "Determination of Graphite in Pig Iron," and Albert L. Colby followed with a talk on "The Selection of Samples for Analysis." He suggested that instruction in sampling be given to undergraduates as a regular part of their training, and that uniform methods of sampling be adopted by practical chemists.

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THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.

THE DECARBONIZATION OF BONE-BLACK.[1]

BY W. D. HORNE, PH.D.

Received April 16, 1895.

THE chief value of the enormous quantities of bone-black annually used in refining sugar, glucose, mineral and other oils, etc., lies in its power to withdraw from solutions the contained organic coloring matters. After the liquid under treatment has run for some time over the bone-black, the absorption of coloring-matters by the latter is seen to diminish, and when this has proceeded to a certain point the supply is cut off, and the bone-black subsequently washed with water, naphtha, or other appropriate solvent, to wash out, as far as possible, the coloring-matters, etc., which have been absorbed by the bone-black. In spite of the most careful washing, however, some carbonaceous matter persistently clings to the char, to remove which the bone-black is heated in closed iron pipes or retorts in kilns, without the access of air. A destructive distillation of the carbonaceous matters results, driving out a large proportion of their substance in gaseous form, but still leaving a small quantity of their carbon deposited in the pores of the grains of bone-black. This accumulation of carbon is quite slow, and the char may be used about a hundred times in refining high-grade sugars before its pores become so thoroughly choked as to destroy its usefulness. The deterioration is more rapid for low-grade sugars, and in refining petroleum the deterioration is so excessive that a dozen treatments will often exhaust the char. Thus the sugar refiner finds his char about exhausted at the end of

[1] Read before the New York Section, April 12, 1895.

the year, and the oil refiner much sooner. Other minor changes take place in the char, of course, but none which can compare in destructiveness to this accumulation of carbon. When it is remembered that about three tons of bone-black are needed in a sugar refinery to each ton of sugar represented in the daily melt, and that while new bone-black costs upward of $40.00 a ton the discarded char brings only about one-third of that price, it will be appreciated what a heavy annual investment the purchase of new bone-black entails.

Some unsuccessful attempts to obviate this difficulty had been made by others, but the distinction of overcoming it belongs to Mr. Moriz Weinrich, who is already world renowned as the inventor of the steam washing centrifugal machine which bears his name. He has recently invented and patented processes and apparatus for radically improving the quality of old bone-black. One process consists of the complete removal of carbon from the bone-black and the artificial introduction of fresh carbon in smaller quantity. The other consists of a uniform partial removal of carbon when that element is excessive. The first is applicable to exhausted char, such as sugar refineries and oil refineries discard. The second is preferable for removing small percentages of carbon from bone-black which has begun to deteriorate through the choking of its pores with carbon, but which has not reached the limit of usefulness. In the first case all of the carbon is burned out by passing the bone-black in a small continuous stream through the inventor's apparatus, a nearly horizontal cylinder of sheet iron, which is heated to a dull red and revolved constantly. The char enters the drum through a central orifice in the head, closing one end, which is slightly higher than the other, and leaves the drum through peripheral openings in the head of the lower end. Within the drum longitudinal projecting ribs serve to expose the bone-black more completely to the hot air in the drum. The air enters at the openings in the lower end of the drum and either wholly or partially oxidizes the carbon in the bone-black; that depending upon the heat of the drum, the volume of air, the amount of bone-black fed into the drum, the speed of turning, etc.

In case the carbon is all removed the mineral frame-work

remains intact with its pores opened up. This bone-black can then be treated with a solution of glue or molasses, or other carbonaceous matter, to thoroughly impregnate it. Then the whole can be rendered thoroughly dry and submitted to destructive distillation in closed retorts without the access of air. The organic matter is hereby charred in the very pores of the grains of bone, and the carbon thus deposited seems to be exactly similar to that originally present. After the above recarbonization the grains must be washed with hot water to remove soluble substances; and then the char is ready for use.

In the case of partial decarbonization only one operation, that of passing through the drum, is necessary, where a high carbon char can be reduced to a low carbon char and the process regulated to remove any percentage required.

Washed char, fresh from the filters and containing those organic matters which are usually destroyed by destructive distillation in retorts or kilns, can be thoroughly cleansed by passing it through this apparatus at a heat below redness, which indicates the possibility of this method's replacing the present purification or revivification in kilns.

These methods have been investigated and tested by the author, both in the laboratory and on a working scale, in their relations to sugar refining, with eminently satisfactory results, as shown below. Some unfavorable results have, at times, appeared, but they have been due to removable causes, or have been so slight as to be negligible in consideration of the great advantages attained.

LABORATORY TESTS ON TOTAL DECARBONIZATION, ETC.

A quantity of old bone-black, discarded from a sugar refinery, and containing in the neighborhood of twenty per cent. of carbon, was heated in the open air until it was burned white. Sufficient low-grade sugar syrup, for its dry substance to be equal to about fifteen per cent. of the weight of the decarbonized char, was diluted with hot water, thoroughly mixed with the burned bone, evaporated to dryness, and the mixture then put into an iron tube, closed at one end, and having only a small vent in the cap at the other end, and heated to a dull red until all the gas was given off. This carbonized bone was then cooled

and washed with water, to remove all soluble matter, and dried. It now resembled new char in appearance, but contained only about five per cent. carbon. Three hundred cc. of this char were put into a liter bottle with 350 cc. of a solution of molasses sugar, 33° Bé. and exponent = 89.2, and heated one and a half hours in a water-bath at 175° F., with frequent agitations. New char was washed similarly and dried, and 300 cc. subjected to the same treatment. The solutions were then filtered off, and while both had been greatly lightened in color, that from the recarbonized char was considerably lighter than that from the new char. The exponent of the former was 93.0; that of the latter 92.4. The char samples were carefully washed and heated in closed tubes, as before, to remove the impurities, and again treated as before. These two samples were submitted to nine successive treatments with very dark sugar solutions, the object being to ascertain whether the artificially carbonized char would stand use as well as ordinary char. It was also found that while both samples deteriorated greatly, owing to the large amount of work which had been put upon them, the treated char was relatively as much better than the other sample, at the end, as it had been at the beginning, so far as color was concerned. The new char had increased the exponent 0.17 per cent. more than the treated char, in the average of the nine tests, but while the new char had removed 66.6 per cent. of the color from the average solution the recarbonized char had removed 83.3 per cent.

FACTORY TESTS ON A WORKING SCALE.

A decarbonizing apparatus was built, consisting of a cylindrical drum of three-sixteenth inch wrought iron, nine and a half feet long by thirty inches diameter, with a central longitudinal shaft by which it is turned. The drum has a slight inclination from the horizontal and is provided with internal longitudinal ribs to raise the char a little way on the ascending side as the drum revolves. The whole is enclosed by brickwork and heated by a fire built beneath its lower end. By means of this, either a total or a partial decarbonization of char can be effected, and the amount to be burned off can be regulated to a nicety by proper adjustment.

Bone-black that had been in constant use nearly a year and containing twelve per cent. of carbon was reduced to nine per cent. of carbon and tested in the laboratory against the untreated char by the above-mentioned filtration process. The original solution used had a color = 200 on an arbitrary scale. The filtrate from the untreated char had a color = 80; that from the treated char had a color = 27.

In another test the original solution had a color of 240.

Filtrate from untreated char	110
" " treated char	20
" " over-treated char (some white grains)	26

The same samples of char, after draining, were treated again with a slightly less amount of sugar solution.

Filtrate from untreated char,	color = 120
" " treated char,	" = 40
" " over-treated char,	" = 50

In the two treatments the untreated char removed 52.5 per cent. of the color, the treated char 87.9 per cent., and the over-treated char 84.5 per cent.

It was thought that these tests extending over one and a half or two hours might show a greater difference between the samples than tests extending over a longer period, and so the following experiment was made. Three hundred cc. of each char were heated at 175°F., with 600 cc. Muscovado sugar solution at 27° Bé. giving the following results:

Original solution had a color = 210

	One and a half hours.	Six hours.
Filtrate from house char	50	12
" " new char	40	10
" " treated char	20	7

showing that the treated char held its own very satisfactorily.

Further, a series of six consecutive treatments of new char, char several months in use, and the same after partial decarbonization was made. Three hundred cc. of each black were heated at 175° F. with 600 cc. Muscovado solution of 27° Bé. for ten hours, being shaken every fifteen minutes. The char was thoroughly washed, and heated in nearly closed tubes after each absorption test. The average color of the liquor going on was 152.5; that coming off was, house char, 22.8; new char, 16.4; treated char,

16.7. The treated char, although a trifle below the new char in the final average, actually deteriorated less during the tests than either of the others, and thus showed a relative improvement at the end of the experiment.

Many tests have been made on the working scale which have demonstrated the superiority of the decarbonized char over old char, and its equality in many respects to new char.

In the first of these tests a filter of house char containing 12.32 per cent. carbon, and another of decarbonized char containing 10.04 of carbon, had equal quantities of the same liquor run over them for a prolonged period, forty-nine and a fourth hours. The average liquor from the house char had a color of 25, while that from the treated char had an average color of only 15; and it was very striking that the difference in color increased as the test proceeded, the latter part of the liquor from the untreated char averaging 50, while the corresponding portion from the treated char averaged only 25. The house char withdrew 79.88 per cent. of the color present, while the treated char withdrew 87.69 per cent.

In another set of filtrations on the working scale, in a sugar refinery, a raw sugar solution, color 120 and 27.7° Bé., and exponent 90.09, was put, in the regular course of running, through filters of char respectively several months old, new, and decarbonized. The average color of that from the old char was 23; from new char, 19; from decarbonized char 18. The exponents scarcely varied, being 92.17, 92.37, and 92.09, respectively.

These are a few of a great many tests both in the laboratory and in the factory made upon char which had been partially decarbonized in a small working model which could not be controlled with the desired nicety. While the average per cent. of carbon in the decarbonized char was 10.04 per cent., or 2.28 per cent. less than in that from which it was prepared, there was a good deal of it which through different causes still contained more than eleven per cent. of carbon, and considerable which had been so over-heated as to be rendered weak as a decolorizer. These two extremes, while giving a favorable-looking average per cent. of carbon, both deteriorate the char for the purposes in hand.

Some improvement having been made in the operation of the decarbonizing drum, which, however, is still far inferior to what the inventor's design calls for, it has been possible to turn out a much more uniform product. The carbon can be reduced to any desired point and kept to within half a per cent. of the requisite figure. Having thus prepared another large quantity of char, sufficient for factory tests, another experiment was made. The carbon this time was reduced from 13.03 per cent. to 10.22 per cent., and two filters filled with these grades were run against each other. The liquor entering had a color of 110. The average of that coming from the untreated char was ten, while that coming from the treated char, all the conditions being carefully kept precisely similar, was only five. From the old char the liquor ran water-white for less than an hour; from the decarbonized char it ran water-white for more than five hours; and at the end of the run the liquor from this filter was only about as dark as that at the middle of the run from the filter of ordinary char.

Now, as to the changes in the bone-black itself: after a partial decarbonization, microscopic examination shows the decarbonization to be uniform throughout the grain. Two analyses made to illustrate the chemical changes may be quoted:

	Before decarbonization.	After decarbonization.
Carbon	12.32	8.90
Calcium carbonate	3.32	3.26
Iron	0.32	0.21
Calcium sulphate	0.904	0.877
Calcium sulphide	0.628	0.494

The most noticeable and, in fact, the most desirable changes are the reduction of carbon, with a corresponding opening of the pores and increase in absorbing power; and the reduction of calcium sulphide, which is very important for sugar refineries, in view of the deleterious action this latter substance exercises upon the sugar.

Numerous experiments showed that the calcium carbonate is not decomposed by the mild heat which suffices for oxidizing the carbon, and the slight decrease indicated above is doubtless due to variations in samples or error of analysis.

The friction of the grains of bone-black against each other in

the drum is so slight that very little dust is formed. Samples taken to represent as nearly as possible the same char before and after treatment showed per cents. of dust as follows:

	Before treatment.	After treatment.
Finer than thirty mesh....	12.56	12.64
" " fifty "	0.96	2.20

The bone-black becomes specifically lighter in proportion to the carbon lost, but this does not show in the determinations of specific gravity, probably because of the grains packing more closely after treatment. This indicates a wearing off of some sharp corners of the grains. A quantity of bone-black which, before treatment, had a sp. gr. = 1.0624, and lost 2.81 per cent. of carbon during treatment, had a sp. gr. = 1.0636 afterward.

As might be expected, the process of opening the choked pores renders the bone-black slightly more friable, as shown by the fact that a sample which, before treatment, gave 1.76 per cent. of dust, by the method described by the author in a previous paper (This JOURNAL, January, 1895), gave 2.84 per cent. after reatment. This, however, is scarcely more than is given by some new bone-blacks.

The great advantages of these inventions, then, are quite apparent. The refiner of oil, sugar, or glucose, who uses large quantities of bone-black need not discard it at a great loss after its pores are choked with carbon and its decolorizing power lost; but he can, by a very simple and inexpensive process, bring it back to its original decolorizing power, when it will last nearly, if not quite, as long as before. But by far the greater advantage is the possibility of preventing its ever getting into bad condition, by submitting it to the decarbonizing process while yet the carbon is only slightly above the normal for new char, and thus keeping it always at its maximum efficiency.

By a careful use of this apparatus it is possible to burn off the organic impurities persisting in bone-black after washing, instead of charing them as in the ordinary method of revivifying, in kilns with the exclusion of air; and it is not at all impossible that the apparatus will, in the near future, supersede the present kilns used in all factories employing large quantities of bone-black.

YONKERS, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

SULPHIODIDE OF LEAD.

BY VICTOR LENHER.

Received March 30, 1895.

ACCORDING to Humefeld (*J. prakt. Chem.*, **7**, 27) Reinsch (*J. prakt. Chem.*, **13**, 130) and Parmentier (*Compt. rend.*, **114**, 299) there exists a chlorsulphide of lead and an analogous bromsulphide of a cinnabar red color, obtained by adding hydrogen sulphide to a solution of lead chloride in hydrochloric acid, or to the corresponding bromide in hydrobromic acid.

As lead iodide dissolves readily in potassium iodide with the formation of the double iodide $PbI_2,2KI$, and with excess of potassium iodide $PbI_2,4KI$, it was found that when working with this salt an iodosulphide of brick-red color and rapidly changing composition was formed when its solution was treated with hydrogen sulphide.

The precipitate formed, when hydrogen sulphide is added to a solution of the double iodide in potassium iodide, is brick-red in color, rapidly changing, on further addition of that reagent, successively through dark red to brown, and finally the black sulphide is obtained which careful examination showed to be free from iodine. Cold water saturated with hydrogen sulphide was added to a strong solution of lead iodide in a saturated solution of potassium iodide; the red precipitate which was obtained was rapidly filtered by means of a suction apparatus, washed with a saturated solution of potassium iodide to remove any PbI_2,KI which possibly may have separated by the dilution; it was then washed with cold water till the reaction for iodine entirely disappeared; absolute alcohol was then added to displace the water, followed by carbon bisulphide to remove any sulphur, after which absolute alcohol was again added, and the precipitate dried by drawing cold air over it.

When $PbI_2,4KI$ is diluted with water, yellow PbI_2,KI separates. The red sulphide was examined very carefully for potassium but none was found.

As the tendency of the substance to decompose into lead sulphide and lead iodide was so great, only small quantities were prepared at one time.

The lead was determined by treatment with nitric acid, followed by a few drops of sulphuric, and was weighed as sulphate. The sulphur was determined only after much trouble, as all attempts to oxidize it caused sulphur to separate. The method employed was treatment with a hot solution of sodium carbonate, which completely converted it into lead sulphide, carbonate, and sodium iodide. This was brought upon a Gooch crucible, washed with water, followed by a little dilute acetic acid to remove the carbonate, again washed with water, after which it was treated with nitric and sulphuric acids, and weighed as lead sulphate.

The iodine was estimated by covering the iodosulphide with an excess of a decinormal solution of silver nitrate; decomposition was then effected by means of nitric acid, and the excess of silver titrated with a decinormal ammonium thiocyanate solution, using ferric alum as an indicator. Analysis gave the reults:

Lead.	Iodine.	Sulphur.
49.06	49.97	1.51
50.16	49.81	1.98
.....	50.24	2.21
.....	50.33	2.17

The results approximate the composition of $PbS,4PbI_2$ which requires:

Lead.	Iodine.	Sulphur.
49.20	48.77	1.53

Hydrogen sulphide gas passed through a saturated solution of $PbI_2,4KI$ in the cold, also gave a brick-red precipitate which, treated in the manner described in the previous experiment, gave on analysis, 49.98 per cent. of iodine.

This method for the preparation of the iodosulphide is very unsatisfactory, as it rapidly darkens even in presence of large excess of the iodide, and from the fact that only a small fraction of a per cent. of product can be obtained.

Various colored products were obtained in the investigation,

containing lead from 49.06 per cent. to the normal sulphide, and iodine in a similar manner from 50.84 per cent. to a sulphide entirely free from it. All of these but the one approximating, $PbS,4PbI_2$, were inconstant in composition and more or less rapidly decomposed into lead sulphide and lead iodide, as might be expected from the knowledge of the chlor- and bromsulphides; the iodosulphide is readily decomposed by heat, acids, and alkalies; and even long exposure to light decomposes it.

ON THE DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID BY THE CITRATE METHOD.[1]

By E. G. Runyan and H. W. Wiley.

Received April 15, 1895.

THE results obtained by analysts in different parts of the world in precipitating phosphoric acid directly by magnesia mixture, in presence of citric acid or its salts, show that this process may safely take the place of the molybdenum method with all standard tricalcium phosphates or their preparations. We have observed in our work the most satisfactory agreement between this method and the molybdenum method of the Association of Official Agricultural Chemists. This statement, however, holds true only when the phosphoric acid is present in considerable quantities, at least in excess of five per cent. With smaller quantities of phosphoric acid we have observed that the citrate method leads to results which are decidedly inferior to those obtained by the molybdenum process.

The principle of the citrate method may be stated as follows: In the presence of a considerable excess of ammonium citrate a solution of a magnesium salt, made alkaline by ammonia, will precipitate the phosphoric acid as ammonium magnesium phosphate. The iron and alumina which may be present in the solution will not be precipitated under the above circumstances either as hydroxides or as phosphates. The ammonium magnesium phosphate can be subsequently separated by filtration, converted into magnesium pyrophosphate and weighed. An examination of the

[1] Read before the Washington Section, April 11, 1895.

pyrophosphate obtained as above will disclose the presence of iron and alumina, but experience has shown that an equivalent amount of phosphoric acid will be found in the filtrate after the separation of the ammonium magnesium phosphate. The errors are, therefore, mutually compensatory and results obtained agree within the ordinary errors of analysis with those of the molybdenum method.

Our experience having shown us that the above principles could not be applied in the presence of small quantities of phosphoric acid we were led to try the following simple expedient: Whenever we had to deal with a small percentage of phosphoric acid, for instance, anything below ten per cent., we added to the solution, before the precipitation, a sufficient quantity of a solution of a phosphate of known strength to bring the total percentage of phosphoric acid in the mixture up to that of a natural tricalcium phosphate of good quality; *viz.*, from fifteen to thirty per cent. In these circumstances we were able to obtain perfectly accurate results, even in cases where less than one per cent. of phosphoric acid was present. The following analytical data will illustrate the character of the work:

Solutions Employed.—No. 1. This is a solution of cottonseed-meal and castor pomace. It is part of a sample sent out last year, by the reporter on phosphoric acid, to the members of the Association of Official Agricultural Chemists.

Nos. 2 to 5 inclusive. These are solutions of natural phosphates containing very small percentages of phosphoric acid, some of them less than one per cent.

Nos. 6 to 10 inclusive. These are preparations made by diluting a standard solution of a superphosphate with water. This superphosphate was a part of a sample sent out by the official reporter for 1894.

Nos. 11 to 17 inclusive. These are natural rock phosphates containing large percentages of phosphoric acid, and the data show the agreement between the direct citrate and the official molybdenum method.

The above solutions for the citrate method were made by treating two grams of the material with fifty cc. of sulphuric acid and

twenty cc. of nitric acid, and boiling until fumes of sulphuric acid began to escape.

CITRATE METHOD.

Solution No.	Direct. Per cent. P_2O_5.	After adding 25 cc. of known phosphate solution. Per cent. P_2O_5.	Calculated for original solution. Per cent. P_2O_5.	Official molybdenum method. Per cent. P_2O_5
1.	1.08	8.93	2.51	2.46
	2.17[1]	8.97	2.55	2.50
	1.53	15.92	2.61	2.49
	2.30[1]	15.76	2.45	2.48
2.	0.76	10.91	0.89	1.02
	0.64	11.10	1.08	1.02
3.	3.76	14.10	4.08	4.08
	3.64	14.16	4.14	3.99
4.	0.32	10.78	0.76	0.77
	0.19	10.91	0.89	0.76
5.	0.25	10.82	0.80	0.88
6.	0.76	11.16	1.14	1.15
	0.96	11.16	1.14	1.15
7.	2.17	12.38	2.36	2.30
	2.36	12.31	2.29	2.31
8.	3.25	13.46	3.44	3.44
	3.25	13.46	3.44	3.46
9.	4.40	14.67	4.65	4.62
	4.47	14.48	4.46	4.59
10.	5.68	15.69	5.67	5.74
	5.29	15.63	5.61	5.77
11.	17.23	....	....	17.29
12.	37.77	....	....	37.77
13.	15.37	....	....	15.44
14.	29.16	....	....	29.22
15.	29.49	....	....	29.47
16.	31.64	....	....	31.64
17.	32.22	....	....	32.15

Explanatory Notes.—With solution No. 1 four determinations were made. In the first and third instances the mixture was allowed to stand twenty-four hours before filtering, while in the third and fourth instances it was allowed to remain for three days. The results clearly show the progressive separation of the crystalline precipitate, almost the full quantity being secured after the lapse of three days. In the first and second instances there was added enough of a solution of rock phosphate to bring the total phosphoric acid up to about nine per cent., while in the third and fourth determinations a solution of a richer rock was added, bringing the total phosphoric acid in the mixture up to about sixteen per cent. There was little difference noted in the

[1] Stood 72 hours.

results. Beginning with solution No. 2, the increase in the content of phosphoric acid was secured by adding measured quantities of a solution of ammonium phosphate of known stength. The results show that a chemically pure phosphate can be used with equal safety in place of solutions of rock phosphate. By a study of the results obtained with solution 10, it is seen that when the content of phosphoric acid reaches about six per cent. the direct method with magnesium citrate gives approximately correct results. It is to be recommended, however, in all cases where the sample contains less than ten per cent., that fortification with a solution of a phosphate of known strength be practiced.

Solutions 11 to 17 inclusive were made from samples of rock phosphate quite rich in phosphoric acid and, therefore, required no fortification. It is seen in all cases that the data obtained by the direct citrate method are almost identical with those secured by the official molybdenum process.

Conclusions.—(1) In all cases of samples of tricalcium phosphate, or acid phosphates made therefrom, containing the usual accompanying substances, the phosphoric acid may be correctly estimated by direct precipitation with magnesium citrate.

(2) In all cases of the analysis of natural rock phosphates containing less than five per cent. of phosphoric acid it is necessary to fortify the solution before precipitation by adding a measured quantity of a solution of phosphoric acid of known strength.

(3) The fortifying solutions employed may be made either from natural tricalcium phosphates or from chemically pure phosphate salts.

(4) The direct precipitation of the phosphoric acid in the presence of ammonium citrate by ammoniacal magnesia mixture is a quicker and less expensive process than the official molybdenum method and leads to results equally accurate.

(5) We have not applied the direct citrate method to the natural iron and aluminum phosphates, and therefore can make no statement in regard to its accuracy in the treatment of such samples.

[Contributions from the Chemical Laboratory of Oberlin College.]

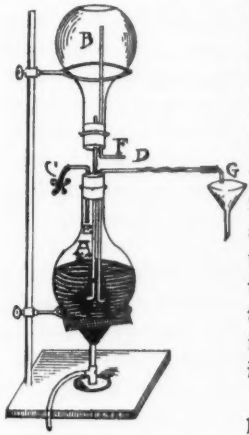
AN ARRANGEMENT FOR WASHING PRECIPITATES WITH BOILING WATER.

By Frank F. Jewett.

Received February 7, 1895.

IN using the ordinary wash-bottle for boiling water, the mouth-piece is not infrequently so much heated by escaping steam that the lips, when applied to it in the usual manner, are either uncomfortably overheated or positively burned. To avoid this result the apparatus, herein described, was devised, and has worked with perfect satisfaction.

Two flasks are arranged as shown in the figure. To the lower one, A, is fitted a rubber stopper through which pass three glass tubes. A short one, bent at right angles, just enters the flask, and to its outer extremity is attached a short rubber tube provided with a spring clip C. A long tube reaches to the bottom of the flask and extends six or eight inches at right angles from a point just above the stopper. To its outer end is attached a rubber tube a few inches long, into which is fitted a glass jet, G, bent at right angles and wound about with a strip of felt or other non-conducting material. A third tube, E, extends from the bottom of the lower flask just through the stopper of the upper flask B, which is also provided with the tube F reaching to the top of the flask.



To use the apparatus, the water is heated to gentle boiling, the steam passing out through the open clip C. When a precipitate is to be washed, the clip is closed and the pressure of the steam at once drives the water out through the tube D. By clasping the non-

conducting cover of the jet G with the thumb and finger, the stream of boiling water may be directed to any place desired. Any excess of pressure simply drives the water slowly through the tube E into the upper flask, from which the air escapes through F.

When a sufficient quantity of water has been used, the clip is opened, the jet G raised, and the water immediately returns to the lower flask.

OBERLIN, OHIO.

INTERPRETATION OF SOME RESULTS IN THE ANALYSIS OF EXTRACTS OF FUSTIC.

BY CHARLES S. BOYER.

Received April 13, 1895.

SOME time since, the writer made several analyses of samples of extract of fustic, the method of whose manufacture was at the time unknown. Since there are no recorded analyses of extracts of fustic, so far as I can find, it was thought that a statement of the results and conclusions might be of interest to those engaged in this line of work.

The method of analysis employed is briefly as follows: Five to six grams of the extract were carefully dried in a water-bath until no further loss occurred, the loss being regarded as water. Two to four grams of this dry powder was now put into a Soxhlet extractor and thoroughly and repeatedly exhaused with *absolute* alcohol, the alcoholic extract distilled, and the residue dried and weighed. The residue was in every case treated with boiling water and tested for *morin* and *maclurin* (*morin-tannin*), the former by adding to one portion a few drops of aluminum sulphate and the latter by adding to another portion some ferric chloride, but in each case with negative results. The residue from the alcoholic extract was ignited in a platinum crucible and the ash subtracted from the matter soluble in absolute alcohol. For the ash percentage, five grams of the powder was carefully ignited in a capacious platinum crucible and the resulting ash weighed.

The results of the analysis of three extracts of fustic found upon the market, together with those of two extracts whose methods of manufacture were known, are put into a table below.

The results are also calculated upon a dry basis so that they may be compared the better.

	I.		II.		III.		IV.		V.	
	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.	Per cent.	On dry basis. Per cent.
Water	67.09	....	50.42	....	36.48	....	49.62	....	6.18	....
Organic matter soluble in absolute alcohol	31.34	95.23	38.57	77.79	52.85	83.20	47.41	94.11	75.55	80.53
Ash	0.52	1.58	5.54	11.18	1.24	1.95	1.05	2.08	7.62	8.12
Organic matter insoluble in alcohol	1.05	3.19	5.47	11 03	9.43	14.85	1.92	3.81	10.65	11.35
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Sample IV was made in an open extractor, the water used in the extraction being brought to a boil before it was run on the wood and the length of time that each "water" remained in contact with the wood being fifteen minutes. Eight "waters" were taken off. Sample V was extracted under five pounds pressure, using seven waters and the weak liquor being evaporated to dryness.

It will be seen that Sample I is very similar to IV, while the analysis of II and V are very much alike, especially in that both have a high percentage of ash and approximately the same amounts of organic matter insoluble in alcohol.

It is quite true that different brands of fustic, and even different cargoes of the same brand, contain varying percentages of inorganic matter, or ash. This might lead one to erroneous conclusions were one to depend entirely upon the ash percentages. However, the chief mineral constituents of fustic are lime and magnesia, and as a result of a large number of analyses the writer finds that these two ingredients form another guide in determining the method of extraction. The more pressure used in the extraction, the higher, within certain limits, the ash percentage, and also the larger the amount of lime and magnesia contained in the ash. In the extracts under investigation the percentages of lime and magnesia together were in I, 41.16 per cent.; IV, 46.83 per cent.; II, 68.12 per cent.; and V, 62.15 per cent. of the total ash.

Another ingredient which might prove misleading is extract of quercitron bark. In order to ascertain whether any of these extracts contained this adulterant, a series of dye-tests were

made depending upon the different affinities of the coloring principles of bark and fustic for alum and tin mordants, but in none of them could any admixture with quercitron bark extract be detected.

The conclusions drawn from these analyses and comparisons were that I was made entirely by the "open-extraction" method; II was made by the "closed-extraction" method, using five to eight pounds pressure; and that III was extracted in open vessels, but that the changes of "waters" was done under pressure. The reason for the latter conclusion was that, while the ash percentage was low, the "extractive matter," or organic matter insoluble in alcohol was very high and the only way that this could happen would be by opening up the fiber of the wood, as is the case in open boiling and then applying pressure, which carried this "extractive matter" into the extracting liquor. These conclusions were subsequently borne out by experiments.

CAMDEN, N. J., April 6, 1895.

THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.

BY FANNY R. M. HITCHCOCK.

[*Continued from page 494.*]

b. Five cc. of the cerium sulphate solution were diluted to sixty cc., and brought to boiling, when alcohol was added, five cc. at a time, until sixty-five cc. had gone in, but the solution still remained clear. To this hot solution the cerium sulphate solution was added in the same way as the alcohol had been. The first addition of five cc. caused a precipitate to form, which redissolved at once. The second addition of five cc. caused a precipitate which dissolved again very slowly, and with the third addition the cerium sulphate came down in fine needles.

It was evident that the amount of alcohol which had been used in experiments 8, 9 and 10, with the sodium molybdate, had not been sufficiently great to cause by itself the precipitation of the cerium sulphate. The experiments were, therefore, repeated, the conditions being slightly varied.

Experiment 11. Ten cc. sodium molybdate solution were diluted to 100 cc., and fifteen cc. of the cerium sulphate solution added. To this, in the cold, fifty cc. of ninety-five per cent. alcohol were added very gradually, and with constant stirring. The

whole was allowed to stand for half an hour, when the precipitate was filtered off, washed, first with fifty per cent. alcohol, then with thirty per cent., and finally with pure water, ignited, and weighed. The results obtained were the best of all the series.

Wt. obtained.	Calculated.	Difference.
0.1620 gram.	0.1629	—0.0009

The ignited precipitate dissolved in hydrochloric acid gave no trace of sulphuric acid when tested with barium chloride.

Experiment 12.—This was a duplicate of No. 11, except that the final washing was done with twenty per cent. alcohol instead of pure water. The washing was continued until there was no reaction with barium chloride for sulphuric acid.

Wt. obtained.	Calculated.	Difference.
0.1799 gram.	0.1629	+0.0170

The precipitate was tested as before, and proved to contain cerium sulphate.

Experiment 13.—Ten cc. of sodium molybdate solution were diluted to 185 cc. and fifty cc. of ninety-five per cent. alcohol added, followed by fifteen cc. of cerium sulphate solution. After standing an hour the precipitate was filtered off, and washed in the same manner as in No. 12.

Wt. obtained.	Calculated.	Difference.
0.1644 gram.	0.1629	0.0015

From the precipitate barium sulphate equivalent to 0.00146 gram of cerium sulphate was obtained, and the filtrate gave 0.0007 gram of molybdenum trisulphide.

Experiment 14.—This was a duplicate of No. 13.

Wt. obtained.	Calculated.	Difference.
0.1708 gram.	0.1629	0.0079

The precipitate yielded the equivalent of 0.0090 gram of cerium sulphate with barium chloride.

With hydrogen sulphide a precipitate of molybdenum trisulphide was given by all the filtrates from the experiments described above, the amount varying in wide limits. While alcohol diminished the solubility of the cerium molybdate formed, the advantage gained was more than counterbalanced by the tendency of the molybdate to carry down with it cerium sulphate in the presence of alcohol.

SODIUM TUNGSTATE AND CERIUM SULPHATE.

The solution of sodium tungstate used contained 27.07 grams in one liter. But few experiments were made, the results obtained being similar to those with sodium molybdate. Precipitation in a water solution alone was very incomplete, the precipitate persistently running through the filter, so that no definite results could be obtained in this way. When alcohol was used better results were obtained, the filtrate coming through clear.

Experiment 1.—Ten cc. sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling when twenty-five cc. cerium sulphate solution were added. A dense, flocculent yellow-white precipitate came down at once, subsiding rapidly; it was filtered and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3266 gram.	0.3144	0.0122

Experiment 2.—Ten cc. of sodium tungstate solution were diluted with distilled water to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added, followed by twenty-five cc. of cerium sulphate solution in the cold. A bluish white precipitate formed, which on standing acquired a yellow tint. This was filtered cold and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3125 gram.	0.3144	—0.0019

Experiment 3.—Ten cc. of sodium tungstate solution were diluted to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling and twenty-five cc. cerium sulphate added. The precipitate was washed with hot twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3322 gram.	0.3144	0.0178

The precipitate from all three solutions contained cerium sulphate, and the filtrates all showed traces of tungsten.

The next salts taken up were the two very rare ones, neodymium chloride and praseodymium chloride. For the material used I am indebted to the courtesy of Professor Waldron Shapleigh, of the Welsbach Light Company, Gloucester, N. J. The material given me consisted of the oxides prepared from the

oxalates by ignition. These oxides are considered by v. Welsbach[1] to be the peroxides, and the formulas Nd_4O_7 and Pr_4O_7 have been assigned to them.

Nd_4O_7 is a light brown powder, while Pr_4O_7 is dark brown, almost black. Both dissolve readily in hydrochloric acid with evolution of chlorine, and form sesquichlorides. Neodymium chloride, Nd_2Cl_6, forms a rose colored solution while the corresponding praseodymium salt is pale green in color. The solutions used were prepared by evaporating the chlorides prepared from the oxides to dryness, taking up with water and again evaporating until all the hydrochloric acid was expelled. The residue was dissolved in water and filtered off from a little insoluble material which was probably a basic salt. About half a gram of the oxide was taken, and from it 100 cc. of the chloride solution was prepared.

The tungstates obtained from these salts by precipitation with sodium tungstate were gelatinous, and very difficult to filter and wash, showing a strong tendency to pass through the pores of the filter-paper.

For this reason a double filter was always used, and even with this precaution it was necessary to use as little pressure as possible with the filter-pump, and yet secure filtration. Even with the filter-pump the washing was very slow, and generally consumed a day at least, sometimes longer, although the quantities of material used were very small. The best results were obtained by washing first by decantation, and then on the filter.

The molybdates are gelatinous when first precipitated, but on heating they gradually become granular, and are then easily filtered and washed.

The neodymium tungstate has a very pale rose tint before ignition, which changes to a lavender color after ignition. The praseodymium tungstate has a decided greenish yellow tint both before and after ignition. The colors of the molybdates were similar to those of the tungstates, but deeper in tint.

The tendency of the precipitates to adhere to the sides of the beaker was a serious source of error at first; particularly after boiling, when it seemed impossible to remove them entirely. If not heated above 70° C. a piece of moist filter will remove the

[1] *Wien. Monatsheft*, 6, 477, 1885.

adherent precipitate better than anything; in most cases it removes it perfectly, while a rubber is useless.

The ignitions were all made with free access of air, and were continued for at least two hours. Apparently no reduction of the molybdic acid takes place, as a second ignition after moistening with ammonium nitrate or with nitric acid, causes no change in the weight.

The solubilities were determined by the Victor Meyer method.[1] It will be noticed that with the praseodymium salts the solubility increases with a rise in temperature, the increase being more marked with the tungstate than with the molybdate.

With neodymium tungstate the solubility decreases as the temperature rises, while with the molybdate it increases under the same conditions. Slight though the solubility is, it is sufficiently great to cause decided error in the results when such small quantities are taken as were used in the experiments here recorded.

It was found very difficult at first, when analyzing the salts, to obtain a constant weight for the oxides, the results being all higher than theory required. The method finally adopted proved very satisfactory. The precipitated oxalate was strongly ignited together with the filter-paper, in a covered platinum crucible, for half an hour, cooled, and moistened with saturated solution of oxalic acid, then ignited again in the covered crucible.

The excess of weight in the earlier analyses being greater than was called for by oxidation to the peroxides, Nd_4O_7 and Pr_4O_7, the following experiments were made to determine how much oxygen would be taken up by the oxides after they had been reduced to the sesquioxides. In the analyses of neodymium molybdate, the theoretical amount required for the quantity taken was 0.0865 gram; the amount obtained was 0.0863 gram. This was heated in a platinum crucible with a Bunsen burner, the flame being applied at the back of the crucible, while the oxide was drawn forward to prevent any action of reducing gases, as far as possible. The cover of the crucible was bent and placed so as to cause a current of air to pass over the oxide.

[1] *Ber. d. chem. Ges.*, **8**, 998, *1875*.

From time to time the crucible was cooled and weighed. The following table shows the gain in weight observed and the length of time for which the heat had been applied. It is assumed that the weight first taken represents the sesquioxide, and the atomic mass is taken as 140.5.

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0863 gram.	0.0000	Nd_2O_3.
4 "	0.0888 "	0.0025	Nd_4O_7.
5 "	0.0892 "	0.0029	
7½ "	0.0906 "	0.0043	Nd_2O_4?
10½ "	0.0937 "	0.0074	
16 "	0.0958 "	0.0095	
22 "	0.0997 "	0.0134	Nd_2O_6?
27½ "	0.1035 "	0.0172	Nd_2O_7?
30½ "	0.1036 "	0.0173	

The oxide on first heating changed to light brown, the color of the superoxide prepared by the Welsbach Company; as the heat was continued it grew lighter in color, until, when it had attained its maximum weight, it was almost pure white.

If the flame be placed directly under the oxide, it loses weight and gradually passes into the brown "superoxide," Nd_4O_7.

A similar experiment with praseodymium sesquioxide, Pr_2O_3, gave the following results:

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0668 gram.	0.0000	Pr_2O_3.
4 "	0.0706 "	0.0038	Pr_2O_4?
6 "	0.0722 "	0.0054	
8 "	0.0730 "	0.0062	Pr_2O_5?
11 "	0.0745 "	0.0077	
13 "	0.0749 "	0.0081	

The atomic mass of praseodymium is taken at 143.5. The color of the oxide changed in the same way as that of neodymium, passing rapidly into the black peroxide Pr_4O_7 of Welsbach, then slowly changing to a reddish brown, and gradually becoming quite light in color. Whether it would be possible to increase the weight still more by heating small quantities for a long period of time, can only be determined by experiment; but the indications point to the existence of praseodymium trioxide PrO_3, as the increase in weight obtained is greater than that required for Pr_2O_5.

It would appear that the oxide Nd_2O_7 can be formed, improbable as it may seem, and that it is comparatively stable.

If it is really Nd_2O_7, neodymium is properly classed with manganese in the seventh group. It would be interesting to know if by reduction the monoxide NdO could also be formed.

SODIUM TUNGSTATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium tungstate contained five grams in one liter.

Experiment 1.—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol were added, followed by five cc. of praseodymium chloride solution in the cold. A precipitate formed at once, and the whole was boiled for an hour. It was then filtered, washed with hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

Wt. obtained.	Calculated.	Difference.
0.0579 gram.	0.0586	—0.0007

Experiment 2.—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of alcohol added. The whole was brought to boiling, and five cc. of the praseodymium chloride solution added, after which the boiling was continued for an hour. The precipitate was then filtered off, and washed with cold water containing twenty per cent. of alcohol. The filtrate showed a slight opalescence, which was not removed by refiltering.

Wt. obtained.	Calculated.	Difference.
0.0540 gram.	0.0586	—0.0046

Experiment 3.—Twenty cc. of the sodium tungstate solution were diluted with seventy-five cc. of distilled water, and five cc. of the praseodymium chloride added. The whole was then boiled for an hour, allowed to cool, and filtered cold, the washing being done with cold water.

Wt. obtained.	Calculated.	Difference.
0.1091 gram.	0.1172	—0.0081

Experiment 4.—Twenty cc. of sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added. The whole was allowed to

stand for twelve hours, then brought to boiling, filtered hot, and washed with boiling water.

Wt. obtained.	Calculated.	Difference.
0.1136 gram.	0.1172	—0.0036

The filtrate was boiled for an hour with fifty cc. of ninety-five per cent. alcohol, but no additional precipitate was obtained.

Experiments 5 and *6*.—Twenty cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added, followed by fifty cc. of ninety-five per cent. alcohol. The whole was then boiled, filtered while hot, and washed with hot water containing thirty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 5.	0.1200 gram.	0.1172	0.0028
" 6.	0.1230 "	0.1172	0.0058

Experiments 7, *8*, and *9*.—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, and six cc. of the praseodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was heated to 60° C. for half an hour, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 7.	0.1733 gram.	0.1758	—0.0025
" 8.	0.1730 "	0.1758	—0.0028
" 9.	0.1724 "	0.1758	—0.0034

The precipitates after ignition showed traces of the blackish-brown praseodymium peroxide Pr_4O_7. The filtrate was tested with hydrogen sulphide, but gave no reaction for tungsten.

Experiments 10, *11*, *12*, *13*, and *14*.—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, six cc. of the praseodymium chloride solution, and twenty-five cc. of alcohol added, and the whole heated for two hours at a temperature of 60° C. The precipitate was filtered off while the solution was hot, and was washed with 150 cc. hot water, containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 10.	0.1715 gram.	0.1758	—0.0043
" 11.	0.1712 "	0.1758	—0.0046
" 12.	0.1713 "	0.1758	—0.0045
" 13.	0.1712 "	0.1758	—0.0046
" 14.	0.1713 "	0.1758	—0.0045

The ignited precipitates appeared to be homogeneous, no traces of Pr_4O_7 showing.

The filtrates were all tested for tungsten with hydrogen sulphide, but no tungsten trisulphide was obtained. This test is not of much value, however, when alcohol is present, as that will prevent the precipitation of tungsten as sulphide to a great extent, so that small quantities will escape detection, unless the alcohol is removed by evaporation before the hydrogen sulphide is used. The precipitaton of molybdenum does not seem to be hindered under the same conditions, the hydrogen sulphide bringing down minute traces in a solution containing thirty-three per cent. of alcohol.

As the error is constant, and the condition of precipitation the same for all the numbers of this series of experiments, it is probably due to the solubility of praseodymium tungstate in water containing alcohol.

ANALYSIS OF PRASEODYMIUM TUNGSTATE.

One-tenth of a gram of the salt was fused with three grams of equal parts of sodium carbonate and sulphur. The fused mass was taken up with water, the gray-green insoluble residue filtered off, and washed with cold water; the filtrate was acidified with hydrochloric acid, the precipitated tungsten trisulphide filtered off on a tared filter, and dried in the air-bath at 100° C. until a constant weight was obtained.

When allowance is made for the molybdic acid present in sodium tungstate the amount of sulphide obtained must be lower than that called for by theory for pure praseodymium tungstate. The praseodymium oxide should be slightly higher in amount.

To estimate the oxide the insoluble residue from the fusion was dissolved in hydrochloric acid, precipitated with oxalic acid and ammonium hydroxide, and ignited in a covered crucible as already described.

	Wt. obtained.	Calculated.	Theoretical.
Pr_2O_3	0.0334 gram.	0.0331	0.0325
WS_3	0.0806 "	0.0808	0.0814

These results leave no doubt but that the constitution of this salt is correctly represented by the formula $Pr_2(WO_4)_3$.

To determine the solubility of the salt, praseodymium chloride

was precipitated by sodium tungstate in aqueous solution; the precipitate with the solution was heated to 60° C. for two hours before filtering, and was washed with hot water until silver nitrate showed no trace of chlorine. The precipitate was dried in the air for a week, and then finely powdered. Portions of the salt were mixed with distilled water at different temperatures, about eighty cc. of water being taken for each portion, and then allowed to stand for two hours, the temperature being kept constant and the liquid frequently stirred. At the end of two hours they were filtered into weighed porcelain crucibles, evaporated to dryness, ignited, and weighed.

The results obtained are given below:

Temperature.	Wt. of solution.	$Pr_2(WO_4)_3$.	Solubility.
20° C.	39.3817 grams.	0.0000	0:00000
20° C.	44.6541 "	0.0000	0:00000
75° C.	44.2312 "	0.0019	1:23300
75° C.	40.1484 "	0.0018	1:22300

SODIUM MOLYBDATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

Experiments 1–6.—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water, then twelve cc. praseodymium chloride solution were added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 65° C. The precipitate was then filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.2093 gram.	0.2101	—0.0008
" 2.	0.2094 "	0.2101	—0.0007
" 3.	0.2096 "	0.2101	—0.0005
" 4.	0.2084 "	0.2101	—0.0017
" 5.	0.2084 "	0.2101	—0.0017
" 6.	0.2080 "	0.2101	—0.0021

The precipitates numbered 1, 2, and 3, all showed traces of praseodymium oxide Pr_4O_7; the others seemed to be homogeneous.

The filtrates were all tested for molybdenum, with zinc, hydrochloric acid and potassium thiocyanate, but none was found. Alcohol does not interfere with the delicacy of this test.

The ignited salt was analyzed, the molybdic acid being determined by the Pechard method, while the praseodymium oxide was determined in the residue, after the molybdic acid was expelled, by the same method as had been pursued with the tungstate.

	Wt. obtained.	Calculated.
WO_3	0.1135 gram.	0.1127
Pr_2O_3	0.0874 "	0.0873

The amount taken for analysis was two-tenths of a gram, and the resuts show the correct formula to be $Pr_2(MoO_4)_3$ corresponding to that found for the tungstate.

The solubility of praseodymium molybdate was determined with the following results:

Temperature.	Wt. of solution.	$Pr_2(MoO_4)_3$.	Solubility.
23° C.	71.4000 grams.	0.0011	1:65820
75° C.	69.8000 "	0.0010	1:69800

PRECIPITATION OF TUNGSTIC ACID WITH NEODYMIUM CHLORIDE.

The solution of sodium tungstate used contained five grams in one liter.

Experiments 1 and 2.—Twenty cc. of the sodium tungstate were diluted to 100 cc. with distilled water and five cc. of the neodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was brought to boiling, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

The filtrates were opalescent, and repeated filtrations failed to render them clear. The precipitates, after ignition, appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.1117 gram	0.1167	—0.0050
" 2.	0.1126 "	0.1167	—0.0041

Experiments 3 and 4.—Ten cc. of the sodium tungstate solution diluted to fifty cc. with distilled water, and three and one-half cc. of neodymium chloride solution added were heated to boiling, filtered while hot, and the precipitate washed with hot water.

	Wt obtained.	Calculated.	Difference.
Experiment 3.	0.0595 gram.	0.0583	0.0012
" 4.	0.0573 "	0.0583	—0.0010

Experiments 5–16.—These experiments were duplicates of 3 and 4, excepting that the solutions were heated to 80° C. instead of to boiling. No alcohol was added, and the precipitates were washed with hot water. The precipitates showed traces of the brown peroxide, Nd_4O_7.

	Wt. obtained.	Calculated.	Difference.
Experiment 5.	0.0575 gram.	0.0583	—0.0008
" *6.*	0.0575 "	0.0583	—0.0008
" *7.*	0.0593 "	0.0583	+0.0001
" *8.*	0.0600 "	0.0583	0.0017
" *9.*	0.0585 "	0.0583	0.0002
" *10.*	0.0586 "	0.0583	0.0003
" *11.*	0.0590 "	0.0583	0.0007
" *12.*	0.0585 "	0.0583	0.0002
" *13.*	0.0585 "	0.0583	0.0002
" *14.*	0.0581 "	0.0583	—0.0002
" *15.*	0.0584 "	0.0583	0.0001
" *16.*	0.0597 "	0.0583	0.0014

Experiments 17 and 18.—Thirty cc. of the sodium tungstate solution were diluted to seventy cc. with distilled water and six cc. of the neodymium chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated to 70° C., filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
Experiment 17.	0.1724 gram.	0.1749	—0.0025
" *18.*	0.1745 "	0.1749	—0.0004

No. 18 showed slight traces of the peroxide Nd_4O_7.

Experiments 19–21.—These were prepared like the preceding solutions Nos. 17 and 18, but were heated to 60° C. instead of 70°. The filtrates showed no trace of molybdenum when tested with zinc, hydrochloric acid, and potassium thiocyanate.

	Wt. obtained.	Calculated.	Difference.
Experiment 19.	0.1731 gram.	0.1749	—0.0018
" *20.*	0.1727 "	0.1749	—0.0022
" *21.*	0.1728 "	0.1749	—0.0021

A comparison of these results shows that the precipitation of tungstic acid by neodymium chloride is practically quantitative. Analyses of the salt made in the same manner as for praseodymium tungstate agreed closely with the theoretical requirements as regarded the neodymium oxide. The tungstic acid was inva-

riably too low, and the different results were too discordant; the tungstic acid, therefore, was determined by difference; the weight of neodymium oxide found was 0.0651 gram, the amount required by theory being 0.0652 gram. From this was deduced the formula $Nd_2(WO_4)_3$ for the salt, which corresponds to the praseodymium tungstate.

The solubilities, determined as for the praseodymium salts, and under similar conditions were as follows:

Temperature.	Wt. of solution.	$Nd_2(WO_4)_3$.	Solubility.
22° C.	42.1032 grams.	0.0008	1:52630
65° C.	41.7117 "	0.0007	1:59580
98° C.	39.6286 "	0.0006	1:66040

SODIUM MOLYBDATE AND NEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 5.1080 grams in one liter.

Experiments 1–5.—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water; seven cc. of the neodymium chloride solution were added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was then heated to 65° C. for two hours, filtered hot, and the precipitate washed with 150 cc. of hot water containing twenty-five per cent. of alcohol.

The ignited precipitates showed no trace of the brown oxide Nd_4O_7, and the filtrates, when tested, gave no reaction for molybdenum.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.1260 gram.	0.1256	0.0004
" 2.	0.1259 "	0.1256	0.0003
" 3.	0.1260 "	0.1256	0.0004
" 4.	0.1259 "	0.1256	0.0003
" 5.	0.1258 "	0.1256	0.0002

An analysis of two-tenths of a gram of the salt made in the same way as the analysis of praseodymium molybdate gave the following results:

	Wt. obtained.	Calculated.	Difference.
Nd_2O_3	0.0863 gram.	0.0865	—0.0002
MoO_3	0.1134 "	0.1135	—0.0001

From these results the formula $Nd_2(MoO_4)_3$ is deduced for neodymium molybdate.

The solubility determinations gave the following results:

Temperature.	Wt. of solution.	$Nd_2(MoO_4)_3$.	Solubility.
28° C.	69.9311 grams.	0.0013	1:53790
75° C.	71.4279 "	0.0022	1:32466

A comparison of the results obtained shows that the precipitation of both tungstic and molybdic acids by neodymium salts is quantitative.

SODIUM TUNGSTATE AND LANTHANUM CHLORIDE.

The solution of sodium tungstate contained five grams in a liter.

Experiments 1 and 2.—Twenty cc. of sodium tungstate solution were diluted to seventy cc. with distilled water, and seven cc. of lanthanum chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 60° C., after which the precipitate was filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol. The filtrate was clear and gave no reaction for tungsten with hydrogen sulphide. The ignited precipitates appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.1143 gram.	0.1160	—0.0017
" 2.	0.1143 "	0.1160	—0.0017

The tungstate before ignition was of a delicate blue, almost white, and after ignition the color deepened slightly. The color of the molybdate was almost the same as that of the tungstate.

ANALYSIS OF LANTHANUM TUNGSTATE.

The first analysis was made by fusing with sodium carbonate and sulphur, then taking up in water, and filtering off the sodium sulphotungstate formed, from the insoluble lanthanum oxide; then decomposing the filtrate with hydrochloric acid and estimating the tungsten from the tungsten trisulphide found.

The results obtained were very satisfactory so far as the lanthanum oxide was concerned, but no good results were obtained for the tungstic acid.

The amount of the salt taken for analysis was one-tenth of a gram.

	Wt. obtained.	Calculated.
La_2O_3	0.0326 gram.	0.0321
WS_3	0.0606 "	0.0822

The same difficulty was encountered here that was met with in the analysis of neodymium tungstate, and the cause was not apparent. A second analysis by a different method was made, the same amount of material being taken. The lanthanum tungstate was decomposed with aqua regia, evaporated to dryness with hydrochloric acid three times, and the separated tungsten trioxide filtered off and dissolved in ammonium hydroxide; the filtrate was rendered ammoniacal, the solution of the tungstic acid added to it, and hydrogen sulphide passed through it until the liquid was deep yellow in color. The liquid was acidified with hydrochloric acid, and before neutralization was complete the color changed to a bright green, becoming red when completely acidified. On rendering it ammoniacal again, the green color reappeared.

Hydrogen sulphide was passed through the solution again for an hour, hydrochloric acid added, and the solution warmed; it gradually became colorless, and a light brown precipitate of tungsten trisulphide settled down.

This was treated in the usual manner and dried at 100° to constant weight.

	Wt. obtained.	Calculated.
WS_3	0.0640 gram.	0.0822

The filtrate was boiled until all the hydrogen sulphide was expelled, a few drops of nitric acid added, and then ammonium hydroxide; the precipitate of lanthanum hydroxide was evidently not pure, being yellow in color instead of white; it was filtered off, ignited, dissolved in aqua regia, evaporated to dryness, taken up with a little hydrochloric acid, followed by ammonia, and the treatment with hydrogen sulphide repeated. The yellow ammoniacal solution passed through the same color changes as before, when acidified. On heating, a dark red-brown precipitate formed which was filtered off, and washed with dilute hydrochloric acid, and then with alcohol. A great part of the precipitate dissolved in the alcohol to a dark red solution, the precipitate left on the filter-paper turning brown. This precipitate was ignited in a weighed porcelain crucible and evaporated with concentrated nitric acid until a constant weight was obtained. It had the appearance of tungstic acid.

Wt. obtained = 0.0073 gram.

The alcoholic filtrate was evaporated to dryness in a weighed porcelain crucible, and treated repeatedly with fuming nitric acid to oxidize any sulphur that might be present to sulphuric acid, which was removed by repeated evaporation with ammonium hydroxide. The substance remaining in the porcelain crucible had the appearance of molybdic acid. It was pale yellow in color, was readily soluble in ammonium hydroxide, and also dissolved in aqua regia to a bright yellow solution, separating out as a bright yellow powder on concentrating the solution. The yellow powder, when ignited, turned brown, but regained its color on cooling, finally, however, becoming lemon-yellow. When moistened with hydrochloric acid and heated, no blue color appeared. A faint orange-red solution was obtained by treatment with zinc, hydrochloric acid, and potassium thiocyanate. Heated on platinum foil with concentrated sulphuric acid no blue color was produced. The phosphorus bead was colorless, even after treating with tin on charcoal.

The weight obtained was 0.0076 gram. The second analysis gives the following results:

	Wt. obtained.	Calculated.
La_2O_3.	0.0326	0.0321
WO_3.	0.0613	0.0679
	0.0076	

This corresponds to the formula $La_2(WO_4)_3$ for lanthanum tungstate. The same salt was prepared by W. French Smith[1] by the precipitation of sodium tungstate with lanthanum salts.

The solubility of lanthanum tungstate in water was determined by the Victor Meyer method, the salt being prepared in the same way as the praseodymium tungstate.

Temperature.	Wt. of solution.	$La_2(WO_4)_3$.	Solubility.
27° C.	60.5580 grams.	0.0007	1:86510
65° C.	42.4678 "	0.0010	1:42467

SODIUM MOLYBDATE AND LANTHANUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

Experiments 1–3.—Twenty cc. sodium molybdate solution were diluted to seventy cc. with distilled water, seven cc. of lantha-

[1] "Ueber Didymium and Lanthanum." Inaugural Dissertation by W. French Smith. Göttingen, 1876.

num chloride solution added, followed by twenty-five cc. of ninety-five per cent. alcohol.

The precipitate, at first gelatinous, gradually became granular, and was filtered off, washed with 150 cc. hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
Experiment 1.	0.2063 gram.	0.2083	—0.0020
" 2.	0.2061 "	0.2083	—0.0022
" 3.	0.2063 "	0.2083	—0.0020

The filtrates were clear and gave no reaction for molybdenum when treated with potassium thiocyanate in the presence of zinc and hydrochloric acid.

The solubility of the salt obtained was determined under the following conditions:

Temperature.	Wt. of solution.	$La_2(MoO_4)_3$.	Solubility.
25° C.	72.5500 grams.	0.0013	1:55800
85° C.	69.3474 "	0.0023	1:30150

ANALYSIS OF LANTHANUM MOLYBDATE.

The analysis was made in the same manner as with the other molybdates, the salt being decomposed in a current of dry hydrogen chloride gas. The molybdic acid was driven off very readily at first, but toward the close of the operation the full heat of the Bunsen burner was required. Two-tenths of a gram of the salt were taken for analysis, and results were as follows:

	Wt. obtained.	Calculated.
La_2O_3	0.0853	0.0856
MoO_3	0.1145	0.1144

From these results the formula $La_2(MoO_4)_3$ may be calculated for lanthanum molybdate.

Tests were now made with thorium chloride, potassium zirconium fluoride, and zirconium fluoride.

With thorium chloride no definite results could be obtained from either sodium molybdate or sodium tungstate; precipitates were formed with both salts even in quite dilute solutions, but they were slight in quantity, and ran through the filter in spite of every attempt to prevent it, whether filtered hot or cold. Neither alcohol nor ammonium salts made any difference in the behavior.

With the potassium zirconium fluoride no precipitate was obtained with either the sodium tungstate or molybdate.

With zirconium fluoride no results were obtained, the solutions remaining clear after standing several days.

Beyond these qualitative tests no work was done with the thorium or zirconium salts in connection with tungsten and molybdenum.

SUMMARY.

1. The tungstates and molybdates are precipitated quantitatively by nearly all the rare earths.

2. A separation of tungstic and molybdic acids is not possible through their combinations with the rare earths.

3. The non-precipitation of molybdic acid by uranyl solutions when tungstates are absent, and the almost complete precipitation of both when tungstic acid is also present is further evidence of the fact that we can scarcely hope to effect this separation by the method of precipitation.

4. The molybdates and tungstates of neodymium and praseodymium are new, and their constitution is correctly represented by the formula $Nd_2(MoO_4)_3$, $Nd_2(WO_4)_3$, and $Pr_2(MoO_4)_3$, $Pr_2(WO_4)_3$.

5. The solubility determinations indicate that tungstates and molybdates of the rare earths must be classed among the more difficultly soluble compounds.

6. Further research is required upon the methods to be followed in the separation of tungstic and molybdic acids from the oxides of the rare earths.

A NEW TABLE FOR THE QUALITATIVE SEPARATION OF THE METALS OF THE IRON GROUP.

By C. L. Hare.

Received April 15, 1895.

IN the qualitative separation of metals of the iron group much trouble has been experienced with the methods in general use for the separation of cobalt and nickel.

The methods commonly used for the separation of iron, aluminum, and chromium are also unsatisfactory.

The following compilation and application of methods recently worked up greatly simplifies and shortens the process for the qualitative separation of the metals of this group.

In the separation of chromium from iron and aluminum advantage is taken of the well-known action of hydrogen peroxide on chromium compounds in presence of an alkali, the insoluble chromium compound being oxidized to soluble chromic acid. (Bauman *Ztschr. anal. chem., 1892* and others.)

The separation of nickel and cobalt, after the removal of manganese and zinc by hydrochloric acid, depends upon the solubility of nickel sulphide in a solution of sodium sulphide, the cobalt sulphide being insoluble in this reagent. (Villiers, *compt. rend.*, **119,** 1263, and **120**, 46.) The sulphides of the two metals are dissolved in aqua regia and the greater part of the acid expelled. The solution is diluted and a slight excess of tartaric acid is added to prevent precipitation of the two metals by sodium hydroxide, which is next added in great excess. Hydrogen sulphide is now passed through the hot solution till no further precipitation occurs. Cobalt sulphide is precipitated and the nickel sulphide is held in solution by the sodium sulphide. The presence of a trace of nickel is indicated by the deep brown or black color which it imparts to the solution. The nickel sulphide is precipitated from this solution by the addition of dilute hydrochloric acid.

The following is an outline of the treatment: To a solution of the metals of the iron group add ammonium chloride and ammonium hydroxide, warm, and filter. Boil the precipitated iron, aluminum, and chromium hydroxides with sodium hydroxide, filter, acidify the filtrate, and add ammonium hydroxide. A white precipitate indicates aluminum. Boil the residue of iron and chromium hydroxides with sodium hydroxide and a few cubic centimers of hydrogen peroxide. Filter; a yellow solution indicates chromium. Acidify filtrate with acetic acid and add lead acetate. A yellow precipitate indicates chromium. Dissolve residue of iron hydroxide in hydrochloric acid and add potassium ferrocyanide. A blue precipitate indicates iron.

To the filtrate from iron, aluminum and chromium hydroxides add freshly prepared ammonium sulphide, heat, and filter. Wash the precipitate with cold dilute hydrochloric acid to dissolve manganese and zinc and treat the washings as usual for these two metals. Dissolve the residue of nickel and cobalt sul-

phides, left after washing with hydrochloric acid, in aqua regia, expel nearly all the acid, dilute, and add slight excess of tartaric acid, and then very great excess of sodium hydroxide. Boil and pass hydrogen sulphide through till no further precipitation occurs, filter immediately. Test the precipitate for cobalt by borax bead. The presence of nickel in the filtrate is indicated by its deep brown or black color. If nickel be absent the filtrate will be yellow or colorless.

If nickel be present add dilute hydrochloric acid to filtrate, filter, and test the precipitate for nickel by borax bead.

The ammonium sulphide should be prepared as recently as possible, as an excess of sulphur in solution causes the solution of a portion of the nickel sulphide.

THE PROTEIDS OF BARLEY.[1]

By Thomas B. Osborne.

Received April 2, 1895.

THE proteids of barley have received little attention on the part of chemists. Mulder[2] states that this grain contains six per cent. of albumin and plant-gelatin; the latter was obtained by extracting barley-meal with hot alcohol, cooling the resulting solution and treating the deposited substance with ether. The composition of this body he gave as follows:

	1	2
Carbon	54.93	54.75
Hydrogen	7.11	6.99
Nitrogen	15.71	15.71
Sulphur	0.57	0.62
Oxygen	21.68	21.93
	100.00	100.00

v. Bibra[3] names albumin, plant-gelatin, and casein as constituents of barley but gives no particulars concerning these bodies further than that they all contain on the average 15.5 to 15.6 per cent. of nitrogen.

Kreusler made an investigation of the proteids of barley, the

[1] From the Report of the Connecticut Agricultural Experiment Station for 1894.

[2] Phys. Chem., I, 306–308.

[3] Die Getreidearten u. das Brod. Nürnberg, *1860*, p. 304.

results of which are given by Ritthausen.[1] Kreusler employed coarsely ground meal and finely ground flour, the latter yielding purer preparations, the results being otherwise the same.

He states that the aqueous extract of the ground seed contains an albumin coagulated by boiling and of the following composition:

Carbon	52.86
Hydrogen	7.23
Nitrogen	15.75
Sulphur	1.18
Oxygen	22.98
	100.00

The extract made with seventy-five per cent. alcohol contains, according to Kreusler, three proteids: gluten-casein, gluten-fibrin, and mucedin.

The gluten-casein separates on cooling the hot alcoholic extract, and when purified by boiling with dilute alcohol and fractionally precipitated from solution in acetic acid has the composition stated below.

1, is not corrected for ash and represents the first precipitation from a turbid solution.

2, is the second precipitation from a clear solution and is corrected for ash.

The cold alcoholic extract contains gluten-fibrin and mucedin.

The composition of these Kreusler gives as follows:

	Gluten-casein.		Gluten-fibrin.		Mucedin.	
	1.	2.	From meal.	From flour.	From meal.	From flour.
Carbon	53.84	53.25	55.23	54.55	53.19	53.97
Hydrogen	7.16	7.13	7.24	7.27	6.65	7.03
Nitrogen	16.63	....	15.49	15.70	16.14	16.98
Sulphur }	....	....	22.04	22.48	24.02	0.68
Oxygen }						21.34
						100.00

These proteids were supposed to be the same as those similarly named and described by Ritthausen as occurring in the wheat kernel.

So far as the writer has been able to learn the preceding summary includes all that has been published hitherto in regard to the proteids of the barley kernel that is now worthy of notice.

[1] Die Eiweisskoerper, etc., Bonn, *1872*, p. 103.

My preliminary examination of barley-meal showed that the seeds contain proteid matters soluble in water, in sodium chloride solutions, and in alcohol, and that after complete extraction with all these reagents there remains a considerable quantity of proteid which can be partly extracted by dilute potash solutions, but the greater part of which is insoluble in any reagent hitherto applied.

The material employed consisted of meal made from two-rowed barley and of a very white barley flour kindly furnished by the Health Food Co., of New York, both of which yielded proteids of the same composition and properties, the preparations derived from the flour, however, being less contaminated with coloring matter than those derived from the meal made from the entire grain, including the ground husk, which was so closely adherent, as to render its removal in the laboratory impossible.

PROTEIDS SOLUBLE IN WATER. LEUCOSIN. PROTEOSE.

As an aqueous extract of any seed, is in reality a dilute saline solution, owing to the salts extracted from the seed, and as the proteid matter soluble in alcohol dissolves to a slight extent in very dilute saline solutions, the proteids properly soluble in water were obtained by extracting the meal with sodium chloride solutions, dialyzing away the salts and filtering off the proteid that thereby precipitated. In this way the proteid matter, soluble in pure water, which had been extracted from the meal was obtained in solution by itself. Three kilos of barley, ground to a fine meal, were treated with nine liters of ten per cent. salt solution, applied in successive portions, the bran being removed by washing on a coarse cloth. The starch and other suspended matter was allowed to settle out and the extract was filtered clear. This solution was then saturated with ammonium sulphate and the precipitate produced, after filtering out, was treated with ten per cent. salt solution. The resulting liquid was filtered clear and dialyzed for five days. The globulin that separated in this process was collected on a filter, the solution was returned to the dialyzer for three days longer, and the very small additional amount of substance that separated was filtered out. The clear solution was then heated in a water-bath to 65°, the water of the bath not exceeding 70°. After an hour the coagulum was filtered

out, washed with warm water, alcohol, and ether, and dried over sulphuric acid. This preparation, 1, weighed 4.15 grams and when dried at 110° had the following composition:

Coagulated Barley Albumin, Leucosin.	*Preparation 1.*
Carbon	53.04
Hydrogen	6.78
Nitrogen	16.84
Sulphur	1.42
Oxygen	21.92
	100.00
Ash	0.29

Another preparation was made by treating two kilos of barley meal with ten per cent. sodium chloride solution, squeezing out in a press and repeating the process on the residue. The filtered extract was saturated with ammonium sulphate, the precipitate dissolved in dilute salt solution, subjected to dialysis and, when freed from chlorides, filtered and heated to 65° in a water-bath of 70°. The coagulum produced was washed thoroughly with hot water, alcohol, and ether, and dried over sulphuric acid. This preparation, 2, weighed two and three-tenths grams and, when dried at 110°, had the following composition:

Coagulated Barley Albumin, Leucosin.	*Preparation 2.*
Carbon	52.67
Hydrogen	6.77
Nitrogen	16.41
Sulphur } Oxygen }	24.15
	100.00
Ash	0.31

As this body separated slowly when its solutions were heated to 65° it was thought possible that more than one albumin was present which; if a fact, might be shown by analysis of preparations, precipitated in successive fractions.

Accordingly six kilos of barley-meal were extracted with ten per cent. salt solution and the clear filtered extract saturated with ammonium sulphate. The precipitate produced was dissolved in brine and the solution, after filtering clear, was dialyzed until all the the globulin had precipitated. It was then again filtered clear and in order to obtain a concentrated solution the filtrate

was saturated with ammonium sulphate, the precipitate formed was dissolved in water, and this solution was filtered clear and dialyzed. After six days only a very little more globulin had separated, which was filtered out, and a portion of the clear solution was tested carefully for its coagulation point. When slowly heated in a double water-bath it became faintly turbid at 39° and but very little more so at 49°. The turbidity then rapidly increased, flocks appearing at 56°. After heating at 56° for twenty minutes the solution was filtered and again heated. Turbidity occurred at 50° and flocks formed at 60°. After heating to 65° and holding at this temperature for some time the solution was filtered and again heated. Thereupon the turbidity took place at 70° and a very few flocks formed at 74°. The solution still had a just detectable acid reaction. The entire solution was then heated with great care to precisely 56° in a large water-bath, the temperature of which did not exceed 57°. After keeping at this temperature for an hour the coagulum was filtered out, washed with hot water, alcohol, and ether, and dried over sulphuric acid. This preparation, 3, weighed 0.36 gram and contained, when dried, without correction for ash, 16.48 per cent. of nitrogen.

The filtrate from preparation 3, was then heated to just 60° for three hours, and the second coagulum filtered off and treated as the first had been. This preparation, 4, weighed four-tenths gram and contained, without correcting for ash, 16.74 per cent. of nitrogen. Another part of this same extract, after freeing from globulin as above described, was dialyzed into alcohol for three days, whereby the solution was concentrated and the proteid partly precipitated. In order to separate the albumin from any proteose thrown down with it, the precipitate produced by alcohol-dialysis was digested with absolute alcohol for three days longer and then washed thoroughly with water. A considerable part of the albumin was thus rendered insoluble in water, and after being further washed with absolute alcohol and ether, was dried over sulphuric acid and found to weigh 0.51 gram. This preparation, 5, contained 16.30 per cent. of nitrogen without correcting for ash.

Another preparation of albumin was made in the same way, in

order to obtain a larger quantity for complete analysis. Six kilos of barley flour were mixed with twenty-eight liters of ten per cent. salt solution and seventeen liters of clear filtrate obtained, which was saturated with ammonium sulphate. The precipitate produced was dissolved as far as possible in ten per cent. salt solution, filtered clear, and in order to reduce the volume of the solution it was saturated with ammonium sulphate, the precipitate dissolved in 1000 cc. of water, and dialyzed until entirely free from globulin. The solution was then filtered and dialyzed into alcohol. After being concentrated, absolute alcohol was added and the precipitate filtered off, washed with absolute alcohol and ether, and dried over sulphuric acid. This preparation, 6, weighed four and one-tenth grams. It was then digested with water and the insoluble matter washed thoroughly with water, alcohol, and ether, dried over sulphuric acid, and had the following composition when dried at 110°:

COAGULATED BARLEY ALBUMIN, LEUCOSIN. *Preparation 6.*

Carbon	52.71
Hydrogen	6.78
Nitrogen	16.93
Sulphur	1.51
Oxygen	22.07
	100.00
Ash	0.50

SUMMARY OF ANALYSES OF COAGULATED BARLEY ALBUMIN—LEUCOSIN.

	1.	2.	3.[1]	4.[1]	5.[2]	6.[3]	Average.
Carbon	53.04	52.67	....	....	....	52.71	52.81
Hydrogen	6.78	6.77	....	....	....	6.78	6.78
Nitrogen	16.84	16.41	16.48	16.74	16.30	16.93	16.62
Sulphur	1.42	24.15	....	....	....	1.51	1.47
Oxygen	21.92					22.07	22.32
	100.00	100.00				100.00	100.00

If this proteid be compared with the leucosin[4] obtained from the wheat and rye kernels, it will be seen that the three are almost identical in composition.

[1] Not corrected for ash.
[2] Not corrected for ash; coagulated by alcohol.
[3] Coagulated by alcohol.
[4] Report of the Connecticut Agricultural Experiment Station, *1893*, p. 179.

LEUCOSIN.

	Wheat.	Rye.	Barley.
Carbon	53.02	52.97	52.81
Hydrogen	6.84	6.79	6.78
Nitrogen	16.80	16.66	16.62
Sulphur	1.28	1.35	1.47
Oxygen	22.06	22.23	22.32
	100.00	100.00	100.00

The aqueous extract of the barley kernel contains also a small quantity of one or more proteoses, but owing to the great difficulties encountered in attempting to separate these, no pure preparations have been obtained.

PROTEID SOLUBLE IN SODIUM CHLORIDE SOLUTION. EDESTIN.

The large amount of gum extracted from barley-meal by salt solution renders it very difficult to prepare the globulin in anything like a pure state. This difficulty is further increased by the readiness with which the globulin passes into the insoluble or albuminate condition and is thus lost for further purification. In only three cases was it possible to redissolve and reprecipitate this proteid in sufficient quantity for analysis. In all the extracts made, a considerable amount of globulin was precipitated by dialysis in the form of minute spheroids. So far as noticed, this globulin resembled, in all respects, that found in wheat and rye. It was readily and completely precipitated from salt solution by dialysis and also by adding acid. When dissolved in ten per cent. sodium chloride solution and heated, turbidity occurred at 90°, but no coagulum formed until the solution was boiled, and then only a small part of the dissolved substance separated.

Three kilos of barley-meal were extracted with ten per cent. salt solution, the filtered extract saturated with ammonium sulphate, and the resulting precipitate filtered out, dissolved in ten per cent. brine, and the insoluble matter removed by filtration after adding a *very* small quantity of two-tenths per cent. potash water in order to neutralize the slight acid reaction of the extract. The solution was then filtered clear and dialyzed for four days. The proteid separated in the form of small spheroids which were filtered out, washed with water, alcohol, and ether, and after drying over sulphuric acid found to weigh 4.02 grams. This

preparation was dissolved in ten per cent. salt solution and again submitted to dialysis. After the proteid had precipitated it was filtered out, washed with water, alcohol, and ether, and the final preparation, 7, when dried at 110°, had the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 7.*

Carbon	51.43
Hydrogen	6.71
Nitrogen	18.14
Sulphur } Oxygen }	23.72
	100.00
Ash	0.48

Again six kilos of barley flour were extracted with ten per cent. salt solution, the filtered extract saturated with ammonium sulphate, the resulting precipitate dissolved in salt solution and dialyzed. The precipitated globulin was again dissolved in ten per cent. salt solution and precipitated a second time by dialysis. One and nine-tenths grams of preparation 8 were obtained, having the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 8.*

Carbon	50.82
Hydrogen	6.76
Nitrogen	18.16
Sulphur } Oxygen }	24.26
	100.00
Ash	0.37

Another preparation was made in the same way, save that after dissolving the ammonium sulphate precipitate in salt solution, the proteids were again precipitated by saturation with ammonium sulphate and redissolved in brine, thus yielding a solution of smaller volume which was then dialyzed. After five days' dialysis, the chlorides having been removed, the precipitated globulin was treated in the usual manner and found to weigh 1.85 grams. This preparation, 9, had the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 9.*

Carbon	50.40
Hydrogen	6.48
Nitrogen	18.00
Sulphur } Oxygen }	25.12
	100.00
Ash	0.44

The foregoing analyses, although not showing the agreement to be desired, are on the whole sufficiently alike to warrant their publication, and for the sake of comparison they are here tabulated.

BARLEY GLOBULIN, EDESTIN.

	7.	8.	9.	Average.
Carbon	51.43	50.82	50.40	50.88
Hydrogen	6.71	6.76	6.48	6.65
Nitrogen	18.14	18.16	18.00	18.10
Sulphur } Oxygen }	23.72	24.26	25.12	24.37
	100.00	100.00	100.00	100.00

In view of the close resemblance in properties and similarity in composition it is the writer's opinion that this globulin is the same as that found in a large number of other seeds and previously described under the name edestin.[1] The following table affords a comparison of the composition of this proteid from its different sources.

EDESTIN.

	Wheat.	Maize.	Hemp-seed.	Castor-bean.	Sqash-seed.	Flax-seed.	Cotton-seed.	Rye.	Barley.
C	51.03	51.71	51.28	51.31	51.66	51.48	51.71	51.19	50.88
H	6.85	6.85	6.84	6.97	6.89	6.94	6.86	6.74	6.65
N	18.39	18.12	18.84	18.75	18.51	18.60	18.64	18.19	18.10
S	0.69	0.86	0.87	0.76	0.88	0.81	0.62 }	23.88	24.37
O	23.04	22.46	22.17	22.21	22.06	22.17	22.17 }		
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

On comparing the above analyses it will be seen that the preparations obtained from the cereals show the greatest deviation from the average of these figures. This is unquestionably due to the fact that in these seeds this substance is present in small

[1] Report Connecticut Agricultural Experiment Station, *1893*, pp. 179 and 216.

quantity and is associated with other bodies so that it has been impossible to prepare it from them in a state of perfect purity.

PROTEID SOLUBLE IN DILUTE ALCOHOL. HORDEIN.

After extracting 500 grams of barley-meal with brine the residue was treated with alcohol added in sufficient quantity to form with the water retained by the meal, an alcohol of approximately seventy-five per cent. After digesting a short time, the meal was squeezed out and again treated with seventy-five per. cent. alcohol, and pressed out. The united alcoholic extracts were then filtered clear, concentrated to small volume on a water-bath cooled, and the proteid thus separated washed thoroughly by kneading with distilled water. The separated substance now presented every appearance of gliadin, the proteid similarly obtained from wheat and rye. It was dissolved in a little dilute alcohol in which it was very readily soluble with the exception of a slight residue of coagulated proteid which rendered filtration extremely difficult. The solution was then precipitated by pouring into absolute alcohol and the precipitate digested with absolute alcohol, rubbed to a powder while still moist with alcohol, and treated with ether. When dried over sulphuric acid this preparation, 10, weighed 4.54 grams, and when dried at 110° gave on analysis the following results:

BARLEY PROTEID, *Preparation 10.*

	I.	II.	Average.
Carbon	53.83	53.93	53.88
Hydrogen	6.72	6.92	6.82
Nitrogen	17.32	....	17.32
Sulphur } Oxygen }	....	....	21.98
			100.00
Ash			0.22

Another extract was made by treating 500 grams of barley-meal with three liters of alcohol of nine-tenths specific gravity applied directly to the freshly ground meal. The extract, which had a red-brown color, was squeezed out in a press and concentrated to about one-eighth of its volume. After standing over night the mother-liquor was poured off from the proteid which had separated in a firm mass on the bottom of the dish.

This was then dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. The resulting precipitate was washed with absolute alcohol, digested with ether, dried over sulphuric acid, and found to weigh 12.3 grams. This preparation, 11, when dried at 110°, had the following composition:

BARLEY PROTEID, *Preparation 11.*

Carbon	53.78
Hydrogen	6.51
Nitrogen	17.27
Sulphur	0.95
Oxygen	21.49
	100.00
Ash	0.19

The remainder of preparation 11 was then dissolved in dilute alcohol and, after filtering clear, poured into distilled water and precipitated by adding a few drops of sodium chloride solution. This substance was again dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. After treating with ether and drying at 110°, this preparation, 12, was analyzed with the following results:

BARLEY PROTEID, *Preparation 12.*

Carbon	53.78
Hydrogen	6.82
Nitrogen	17.16
Sulphur	0.93
Oxygen	21.31
	100.00
Ash	0.86

Three kilos of barley-meal were treated with ten per cent. salt solution and washed on a coarse cloth until only the bran and larger particles of meal remained. This residue was then extracted with alcohol of nine-tenths specific gravity, yielding a deep red solution, which was filtered through animal charcoal; but only a part of the coloring-matter was removed. The clear solution was next concentrated on a water-bath, poured into absolute alcohol, and the resulting precipitate digested with absolute alcohol and treated with ether, giving preparation 13, weighing thirty grams and, when dry, having the following composition:

BARLEY PROTEID, *Preparation 13.*

	I.	II.	Average.
Carbon	53.80	53.70	53.75
Hydrogen	....	6.78	6.78
Nitrogen	17.48	17.33	17.41
Sulphur	0.93	....	0.93
Oxygen	....	....	21.13
			100.00
Ash			0.25

A portion of the solution from which preparation 13 had been obtained was precipitated separately by pouring into strong alcohol and adding a few drops of salt solution. The precipitate was treated in the usual manner and gave a preparation, 14, containing much less coloring-matter than the preceding and having the following composition:

BARLEY PROTEID, *Preparation 14.*

Carbon	54.32
Hydrogen	6.74
Nitrogen	17.13
Sulphur } Oxygen }	21.81
	100.00
Ash	1.43

The starchy portion of the barley-meal which had been washed through the cloth, as described, was thoroughly extracted with salt solution and then with dilute alcohol, the extraction being repeated until the proteid was completely removed. The united extracts were filtered and concentrated to two-thirds of their volume by distillation when the solution was poured into a dish and the evaporation continued. The proteid separated as a skin on the surface of the liquid and as a solid mass on the bottom of the dish. When reduced to about one-half the volume of the original liquid the hot mother-liquor was decanted from the separated proteid which formed a tough mass of a pink color. This was washed with water and redissolved in dilute alcohol, giving a deep red solution which was poured into absolute alcohol and the mass of substance that separated was cut up with scissors into small pieces and digested with absolute

alcohol and with ether. When dried over sulphuric acid this preparation, 15, was pinkish in color and weighed thirty grams. Dried at 110° and analyzed the following results were obtained:

BARLEY PROTEID, *Preparation 15.*

Carbon	54.00
Hydrogen	6.72
Nitrogen	17.49
Sulphur } Oxygen }	21.79
	100.00
Ash	0.95

The mother-liquor decanted from preparation 15, was still further concentrated and allowed to cool over night. Only a little substance separated which, however, was washed with water, redissolved in dilute alcohol, and precipitated by pouring into much distilled water to which a little salt had been added. On standing about thirty-six hours the milky solution cleared and the proteid was found in a transparent layer at the bottom of the vessel. After treating with absolute alcohol and ether and drying over sulphuric acid, preparation 16 was obtained weighing seven grams and having when dried, the following composition:

BARLEY PROTEID, *Preparation 16.*

Carbon	53.90
Hydrogen	6.63
Nitrogen	17.08
Oxygen } Sulphur }	22.39
	100.00
Ash	0.23

As this proteid resembled gliadin so closely in its physical and chemical properties it seemed important to subject it to very thorough fractional precipitation in order to determine whether it was a mixture of gliadin with another body or a new, distinct proteid. Another extract was made by treating three kilos of freshly ground barley-meal with ten per cent. salt solution, squeezing out in a press, and treating the residue again in the same way. The meal residue was then mixed with alcohol in

quantity sufficient to make, with the water retained by the meal, an alcohol of about forty per cent. After squeezing out the liquid, alcohol was again added to the residual meal sufficient to increase the strength of the solvent to seventy-five per cent. After digesting for some time the extract was squeezed out and found less colored than the first dilute alcohol extract. This second extract was concentrated by distillation to small volume and cooled giving a deposit of proteid much whiter than any previously made. The mother-liquor from this precipitate was poured into absolute alcohol and a second precipitate obtained. The two precipitates, when united, dehydrated in the usual way, treated with ether, and dried over sulphuric acid, weighed twenty-two grams. Dried at 110° this substance had the following composition:

BARLEY PROTEID, *Preparation 17.*

Carbon	54.30
Hydrogen	6.67
Nitrogen	17.47
Sulphur	0.84
Oxygen	20.72
	100.00

About eighteen grams of this preparation were dissolved in alcohol of 0.9 specific gravity and absolute alcohol was added until a considerable precipitate resulted, when the mixture was heated on a water-bath until the precipitate dissolved. The solution was then cooled and after standing some time the mother-liquor was decanted from the separated substance. This precipitate was marked I. The solution decanted from I, was further treated with absolute alcohol and a second precipitate II, obtained in the same way. The mother-liquor from II was mixed with a large quantity of absolute alcohol and, as the proteid did not separate, a few drops of salt solution were added and the resulting precipitate III filtered off and treated with absolute alcohol and ether in the usual manner.

In the first place, precipitate I was dissolved in a small quantity of seventy-five per cent. alcohol and absolute alcohol was added until the precipitate began to reappear. The whole was heated until the precipitate again dissolved whereupon the solu-

tion was cooled. The substance which separated settled out leaving the solution milky. The mother-liquor was decanted from the small amount of deeply colored proteid which adhered to the bottom of the beaker, and this deposit was dissolved in a little seventy-five per cent. alcohol, treated with absolute alcohol, and the opalescent solution so produced mixed with a little ether. This gave a very small precipitate, almost black in color and very sticky. The solution decanted from this small deposit was treated with a drop of potassium acetate solution and the resulting precipitate, after washing with absolute alcohol and ether, dried over sulphuric acid. It formed a light pink powder, preparation 18, weighing 0.65 gram and when dry contained, ash-free, 16.60 per cent. of nitrogen. Its ash content was 1.04 per cent. The mother-liquor, decanted from the first precipitation of 18, was treated with a drop of potassium acetate solution and the precipitate produced allowed to settle. After standing, the substance settled out and adhered to the bottom of the beaker in a solid mass, from which the clear supernatant solution was decanted. This solution after treatment with absolute alcohol yielded a precipitate which, washed with absolute alcohol and ether, and dried, formed preparation 19, weighing 1.79 grams and having the following composition:

BARLEY PROTEID, *Preparation 19.*

Carbon	53.85
Hydrogen	6.69
Nitrogen	17.22
Sulphur } Oxygen }	22.24
	100.00
Ash	0.40

The substance deposited after the addition of potassium acetate to the solution from which 19 was derived, was dissolved in seventy-five per cent. alcohol, absolute alcohol added to the solution, and the resulting precipitate dissolved by heating. On cooling, a part of the proteid separated and after this had settled, the liquid was decanted and mixed with absolute alcohol, and on treating the precipitate in the usual manner preparation 20 was obtained, which when dried weighed 1.18 gram and gave the following results on analysis:

BARLEY PROTEID. *Preparation 20.*

Carbon	54.33
Hydrogen	6.81
Nitrogen	16.93
Sulphur } Oxygen }	21.93
	100.00
Ash	0.58

The substance deposited by cooling the solution from which 20 was obtained was only partly soluble in dilute alcohol. It was accordingly treated with seventy-five per cent. alcohol and allow to stand until the insoluble matter had settled out. The clear liquid was then decanted and completely precipitated with absolute alcohol. The separated substance was washed with absolute alcohol and ether and when dry weighed 0.81 gram. This preparation, 21, contained, ash-free, 16.65 per cent. of nitrogen and 0.32 per cent. of ash. The insoluble matter just described, after washing by decantation with seventy-five per cent. alcohol, was treated in the usual manner and yielded preparation 22, weighing 1.56 grams and having the following composition:

BARLEY PROTEID. *Preparation 22.*

Carbon	53.91
Hydrogen	6.77
Nitrogen	17.00
Sulphur } Oxygen }	22.32
	100.00
Ash	0.71

Precipitate II was dissolved in a little seventy-five per cent. alcohol and the solution mixed with absolute alcohol. The resulting precipitate (*a*) was dissolved by heating and the solution cooled, whereupon a part (*b*) of the proteid was precipitated. The supernatent solution was poured off, mixed with absolute alcohol, and this precipitate (*c*) which contained all the proteid remaining was dehydrated with absolute alcohol and washed with ether, giving preparation 23, weighing two and

two-tenths grams and having, when dry, the following composition:

BARLEY PROTEID. *Preparation 23.*

	I.	II.	Average.
Carbon	54.63	54.68	54.65
Hydrogen	6.62	6.50	6.56
Nitrogen	17.16	.....	17.16
Sulphur } Oxygen }	.....	.....	21.63
			100.00
Ash			0.32

The substance (*b*), deposited on cooling the solution as above described, was dissolved in seventy-five per cent. alcohol and partly precipitated by adding absolute alcohol. After redissolving the precipitate by the application of heat, the solution was cooled and allowed to stand some time to deposit the precipitate which formed. The liquid was then decanted and the separated substance treated with absolute alcohol and ether, yielding preparation 24, weighing 3.11 grams and having the following composition after drying at 110°.

BARLEY PROTEID. *Preparation 24.*

Carbon	54.27
Hydrogen	6.67
Nitrogen	17.39
Sulphur } Oxygen }	21.67
	100.00
Ash	0.32

To the solution from which 24 separated, absolute alcohol was added in considerable quantity and the proteid thus thrown down was dehydrated with absolute alcohol and washed with ether. When dried this preparation, 25, weighed 0.87 gram and, without correction for ash, contained 17.28 per cent. of nitrogen.

Precipitate III was treated with absolute alcohol and with ether, and dried over sulphuric acid. It weighed 1.63 grams and its composition after complete drying was:

BARLEY PROTEID. *Preparation 26.*

Carbon	53.39
Hydrogen	7.02
Nitrogen	17.49
Sulphur } Oxygen }	22.10
	100.00
Ash	0.59

If these figures are compared it will be seen that no fractional separation has been effected, the variations in the results being no greater than in the preparations previously described. Preparation 18 is low in nitrogen, but this is doubtless due to its containing nearly all the impurities precipitable from the solution. Preparation 21 is also low in nitrogen but this was the most colored of all the preparations and as it was also small in quantity the accuracy of the analysis could not be confirmed. Excluding these two preparations the results agree fairly as shown by the following table:

SUMMARY OF THE PRECEDING FRACTIONAL PRECIPITATES.

	19.	20.	22.	23.	24.	25.	26.	Original substance 17.
Carbon	53.85	54.33	53.91	54.65	54.27	....	53.39	54.30
Hydrogen	6.69	6.81	6.77	6.56	6.67	....	7.02	6.67
Nitrogen	17.22	16.93	17.00	17.16	17.39	17.28	17.49	17.47
Sulphur } Oxygen }	22.24	21.93	22.32	21.63	21.67	....	22.10	21.56
	100.00	100.00	100.00	100.00	100.00		100.00	100.00
Weight	1.79	1.18	1.56	2.2	3.11	0.87	1.63	18.00

As all the preceding preparations were made by extracting barley-meal which contained a large quantity of bran, they were much contaminated with coloring-matter.

In order to obtain products free from color 880 grams of fine ground "pearled barley" (a commercial preparation of barley made by rubbing off the outer coat of the grain), were treated with salt solution, and after squeezing out the excess of liquid, the residue was digested with seventy-five per cent. alcohol. The extract was then filtered, concentrated to small volume, cooled, and the mother-liquor decanted from the separated proteid. This was then dissolved in dilute alcohol, the solution

poured into distilled water, and the proteid thrown down by adding a little salt. The precipitate was again dissolved in a small amount of dilute alcohol and reprecipitated by pouring into absolute alcohol, digested with absolute alcohol for some time, then with ether, dried over sulphuric acid, and found to weigh eight grams. This preparation, 27, was pure white and had the following composition when thoroughly dried:

BARLEY PROTEID. *Preparation 27.*	
Carbon	54.37
Hydrogen	6.81
Nitrogen	17.33
Sulphur	0.88
Oxygen	20.61
	100.00
Ash	0.48

Another preparation was made by extracting six kilos of barley flour with salt solution and then treating the residue with alcohol added in sufficient quantity to make with the water of the brine, which still adhered to the meal, as nearly as possible seventy-five per cent. alcohol. After standing over night the extract was filtered off, concentrated to about one-third its original volume, and cooled slightly. The proteid that now separated out from the hot solution was removed from the liquid, rinsed with water, dissolved in a very little dilute alcohol to a thick syrup, and reprecipitated by pouring into absolute alcohol. The substance was then cut up into small pieces and digested with absolute alcohol and also with ether. When dried over sulphuric acid seventy-eight grams of a pure white preparation were obtained. Twenty-five grams of this were then dissolved in seventy-five per cent. alcohol and the clear solution poured into a large volume of distilled water. A part of the substance separated, leaving the liquid milky. The milky solution was decanted from the separated substance and the latter was washed with water in which some of it dissolved. The turbid liquid and washings were united and precipitated with a little salt solution. After standing over night the proteid separated as a transparent viscid liquid on the bottom of the vessel in the same way as gliadin does under similar conditions. After decanting the supernatant

liquid the deposit was dissolved in dilute alcohol and precipitated by pouring its solution into absolute alcohol. The separated proteid was then digested with absolute alcohol and with ether, and dried over sulphuric acid. A pure white preparation, 28, resulted, which when dried at 110° had the following composition:

BARLEY PROTEID. *Preparation 28.*

Carbon	54.02
Hydrogen	6.79
Nitrogen	17.38
Sulphur	0.84
Oxygen	20.97
	100.00
Ash	1.00

The mass which separated on pouring the alcoholic solution into water, as above described, was dissolved in seventy-five per cent. alcohol and, as it contained a little insoluble proteid which rendered filtration impossible, the solution was allowed to stand over night. The clear supernatant solution was then poured off and concentrated to about one-third of its volume and cooled. The proteid which separated was again dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. After thorough dehydration with absolute alcohol and digestion with ether, the substance was dried over sulphuric acid and yielded preparation 29, which was white in color and weighed 5.46 grams. This substance, when dried, had the following composition:

BARLEY PROTEID. *Preparation 29.*

	I.	II.	Average.
Carbon	54.48	54.54	54.51
Hydrogen	6.70	6.79	6.75
Nitrogen	17.22	17.18	17.20
Sulphur } Oxygen }	21.60	21.49	21.54
	100.00	100.00	100.00
Ash			0.32

Another preparation was made without heating, by pouring a part of the original extract from which preparations 28 and 29 were derived into a large amount of distilled water and allowing

the separated substance to deposit. After some time this settled and the supernatant liquid was poured off, the precipitate washed with water, dissolved in cold dilute alcohol, and the solution poured into absolute alcohol. The precipitate produced was digested with absolute alcohol and then with ether and dried over sulphuric acid, yielding a pure white preparation having, when dry, the following composition:

BARLEY PROTEID. *Preparation 30.*	
Carbon	54.23
Hydrogen	6.83
Nitrogen	17.27
Sulphur	0.75
Oxygen	20.92
	100.00
Ash	0.17

In order to obtain a larger quantity of a colorless preparation, five kilos of barley flour were treated with 10.5 liters of seventy-five per cent. alcohol, and after standing some time the extract was filtered off and six liters of clear solution obtained. This was then concentrated to one-third its volume and rapidly cooled. The proteid separated as a bulky plastic mass, which, after decanting the mother-liquor, was macerated with about 500 cc. of distilled water, the washings were poured off, and the mass of proteid dissolved in 500 cc. of seventy-five per cent. alcohol, yielding a solution of a pale yellowish brown tint. This solution was poured in a thin stream into a quantity of distilled water, and the separated proteid, after removal from the liquid, was again dissolved in seventy-five per cent. alcohol, and the perfectly clear solution poured in a small stream into a large quantity of absolute alcohol. As the soluble salts had been almost completely removed the proteid did not separate even after admixture of 800 cc. of absolute ether. Three or four cc. of salt solution were therefore added to the milky liquid, and an immediate precipitate resulted which rapidly settled, leaving the solution clear and free from proteid, This mixture of absolute alcohol and ether retained all the fat present in the proteid before precipitation, and also some coloring-matter, the liquid being yellow. The solution was decanted and the voluminous precipitate treated with successive portions of absolute alcohol, and

obtained as a snow-white granular substance, weighing, when dried over sulphuric acid, ninety-three grams. This preparation, 31, had the following composition when dried at 110°:

BARLEY PROTEID. *Preparation 31.*

	I.	II.	Average.
Carbon	54.18	54.31	54.25
Hydrogen	6.98	6.65	6.82
Nitrogen	17.20	17.30	17.25
Sulphur	0.84	....	0.84
Oxygen	....	....	20.84
			100.00
Ash			0.09

In order to make certain that this proteid, which so closely resembled gliadin in every respect but composition, was not that substance contaminated with fat, a portion of this preparation was ground to a very fine powder and washed for a long time with hot ether in an extraction apparatus. Only a trace of substance was removed by this treatment, and the proteid after drying, had the same composition as before, as the following figures show:

BARLEY PROTEID. *Preparation 32.*

Carbon	54.20
Hydrogen	6.58
Nitrogen	17.07
Sulphur	0.91
Oxygen	21.24
	100.00
Ash	0.25

Another portion of 31 was dissolved in two-tenths per cent. potash water, yielding a clear solution, which was precipitated by neutralization with two-tenths per cent. hydrochloric acid. The precipitate was washed with water, dehydrated with absolute alcohol, washed with ether, and analyzed with the following results:

BARLEY PROTEID. *Preparation 33.*

Carbon	54.21
Hydrogen	6.87
Nitrogen	17.12
Sulphur	0.76
Oxygen	21.04
	100.00
Ash	0.25

Preparation 31 was then subjected to fractional precipitation in order to make sure that it was not a mixture of two or more

proteids. Twenty-five grams were dissolved in 300 cc. of alcohol of 0.865 sp. gr. by heating on a water-bath, and the solution was quickly cooled. After adding a few drops of ten per cent. salt solution the most of the proteid separated in a coherent mass, leaving the liquid clear. After decantation, the residue was treated in the same way again, the decanted solutions being united. The residue was again dissolved and absolute alcohol added to the hot solution until a considerable precipitate resulted, when it was heated until clear and then cooled. A few drops of salt solution were then added and the proteid precipitated, leaving the solution slightly milky. This liquid was joined to the two solutions from which the proteid had been previously separated, and a little more salt solution added to the mixture, thereby precipitating the remainder of the dissolved proteid. After decanting the liquid from the separated substance the latter was treated with absolute alcohol and gave preparation 34, representing the fraction soluble in the strongest alcohol and having, when dry, the following composition:

BARLEY PROTEID. *Preparation 34.*

Carbon	54.32
Hydrogen	6.78
Nitrogen	17.02
Sulphur	0.94
Oxygen	20.94
	100.00
Ash	0.21

The proteid, which had been precipitated during the preparation of this substance as just described, was dissolved in alcohol of 0.865 sp. gr., and the solution cooled rapidly by immersing in cold water. When a part of the substance had separated the solution was decanted and the separated substance treated with absolute alcohol. Preparation 35 was thus obtained, which gave the following figures on analysis:

BARLEY PROTEID. *Preparation 35.*

Carbon	54.47
Hydrogen	7.01
Nitrogen	17.15
Sulphur	0.74
Oxygen	20.63
	100.00
Ash	0.43

The above preparation represented the portion least soluble in strong alcohol. The solution decanted from this preparation was precipitated with absolute alcohol and a few drops of salt solution, and the resulting precipitate, after the usual treatment, yielded preparation 36, having the following composition:

BARLEY PROTEID. *Preparation 36.*

Carbon	54.37
Hydrogen	6.81
Nitrogen	17.30
Sulphur	0.84
Oxygen	20.68
	100.00
Ash	0.38

The following table includes all analyses of the preparations which were free from coloring-matter.

HORDEIN. BARLEY PROTEID SOLUBLE IN DILUTE ALCOHOL.

	27.	28.	29.	30.	31.	32.
Carbon	54.37	54.02	54.51	54.23	54.25	54.20
Hydrogen	6.81	6.79	6.75	6.83	6.82	6.58
Nitrogen	17.33	17.38	17.20	17.27	17.25	17.07
Sulphur	0.88	0.84	21.54	0.75	0.84	0.91
Oxygen	20.61	20.97		20.92	20.84	21.24
	100.00	100.00	100.00	100.00	100.00	100.00

	33.	34.	35.	36.	Average.
Carbon	54.21	54.32	54.47	54.37	54.29
Hydrogen	6.87	6.78	7.01	6.81	6.80
Nitrogen	17.12	17.02	17.15	17.30	17.21
Sulphur	0.76	0.94	0.74	0.84	0.83
Oxygen	21.04	20.94	20.63	20.68	20.87
	100.00	100.00	100.00	100.00	100.00

This body differs essentially from all the well-defined plant proteids now known. As it appears to be characteristic of barley, I propose to adopt for it the latterly disused name *hordein*, which was first applied about 1870 by Proust[1] and ten years later by Hermbstädt[2] to certain products of their attempts to isolate the proximate principles of this cereal.

Hordein appears to have been obtained nearly pure from bar-

[1] Ann. chim. phys., 5, 337.
[2] J. tech. Chem., 12, 46.

ley flour by Kreusler, as shown by the following comparison of his analysis with the average above given.

BARLEY PROTEID SOLUBLE IN DILUTE ALCOHOL.

	Kreusler.	Osborne.
Carbon	53.97	54.29
Hydrogen	7.03	6.80
Nitrogen	16.98	17.21
Sulphur	0.68	0.83
Oxygen	21.34	20.87
	100.00	100.00

Ritthausen regarded this proteid as identical with the mucedin believed by him to occur in wheat and rye, but which, as my investigations prove, does not exist in those grains.

Toward water my different preparations of hordein behave somewhat differently. Preparations dried over sulphuric acid and still retaining a little alcohol dissolve in cold water to a greater or less extent according to the amount of alcohol present. When dried completely at 110°, so that all the alcohol is removed, very little hordein dissolves in cold water and slightly more on raising the temperature. Solutions thus made with hot water do not precipitate on cooling or coagulate on boiling although they give no inconsiderable precipitates on adding salt. A large number of preparations of this proteid and of wheat gliadin were thus tested and compared under similar conditions. The gliadin showed variations in solubility in the same way as the barley proteids, but throughout was much more soluble than the latter, yielding solutions with warm water which were precipitated by cooling. As drying at 110° tends to render more or less of these proteids insoluble in seventy-five per cent. alcohol it is not possible to say definitely whether the difference was due to original difference in properties of the two proteids tested or to the drying. It is the opinion of the writer that the hordein of barley is decidedly less soluble in water than the gliadin of wheat.

Toward alcohol the hordein behaves, so far as could be detected, exactly like gliadin. In very dilute acids and alkalies it is readily soluble and is precipitated by neutralization. Dissolved in concentrated hydrochloric acid a beautiful crimson color is produced similar to that given by gliadin under like

conditions. With a warm mixture of equal volumes of water and concentrated sulphuric acid a red color is given by hordein, not a purple red as by gliadin.

The most marked difference between hordein and gliadin is in composition, since hordein contains one and a half per cent. more carbon, one and a half per cent. less nitrogen, and three-tenths per cent. less sulphur than gliadin.

In the extraction last described 5000 grams of barley flour were treated with 10.5 liters of alcohol, and the extract obtained measured six liters, which was equivalent to 57.1 per cent. of the whole solution employed. If we assume, as is very nearly true, that this was equal to a complete extraction of 57.1 per cent. of the flour, the proteid obtained was equivalent to all the alcohol soluble proteid contained in 2855 grams of flour. In addition to the ninety-three grams of proteid above described, there was obtained a further quantity weighing, when thoroughly dried over sulphuric acid, 17.5 grams, thus making in all 110.5 grams. This quantity is 3.87 per cent. of the 2855 grams extracted. In order to confirm these figures 500 grams of barley flour were extracted with two liters of hot seventy-five per cent. alcohol, squeezed out in a press and the residual meal treated again in the same way with another liter of alcohol and the united extracts filtered clear and concentrated by evaporation. All the proteid contained in the solution separated on cooling and was washed with ether, then dehydrated with absolute alcohol, again digested with ether, and dried completely over sulphuric acid. Twenty and two-tenths grams of proteid were thus obtained equal to 4.04 per cent of the flour. We may therefore assume that this barley flour contained about four per cent. of the alcohol-soluble proteid, hordein.

PROTEID INSOLUBLE IN WATER, SALINE SOLUTIONS, AND ALCOHOL.

The proteids thus far described form only a part of the total proteids of the seed. One hundred grams of barley flour were extracted, first, with a large excess of five per cent. salt solution and then, repeatedly, with hot seventy-five per cent. alcohol. The residue, washed with absolute alcohol and thoroughly air-dried, weighed seventy-one grams and contained 1.07 per cent.

of nitrogen. The air-dry flour, before extraction, contained 1.83 per cent. of nitrogen. The 100 grams of flour therefore contained 1.83 grams of nitrogen and the residue, after extraction, contained 0.76 grams. The nitrogen removed by the solvents therefore amounted to 58.3 per cent. of the whole.

If we assume that the nitrogen all belonged to proteid-matter containing seventeen per cent. of nitrogen, the flour included 10.76 per cent of proteids, of which 58.3 per cent. was soluble in the reagents used in extracting the proteids already described. We have therefore 10.76—6.28 = 4.48 per cent. of proteid unextracted. It was only possible to obtain this proteid by treating the residue with potash water. All attempts, however, to thus prepare it in quantity sufficient to yield preparations of even approximate purity resulted in complete failure.

The previous extraction of the flour to remove the proteids already described seemed to render, to a great extent, the remaining proteid insoluble in potash water and only insignificant precipitates resulted on neutralizing the extracts. The barley flour also contained a large quantity of gum which rendered the filtration of the alkaline extract very difficult, as this gum dissolved freely in potash water. As the proteids prepared from the barley flour are all so similar to those obtained from wheat flour it is most probable that this seed also contains a considerable quantity of proteid soluble only in dilute alkaline solutions, but, as in the case of rye, the writer was unable to obtain results of any value whatever in regard to it.

CONCLUSION.

The barley kernel contains:

I. Leucosin coagulating at 52°, which is the same as the albumin found in the wheat and rye kernels. Its composition, as shown by the average of six analyses, is:

Carbon	52.81
Hydrogen	6.78
Nitrogen	16.62
Sulphur	1.47
Oxygen	22.32
	100.00

This substance forms about three-tenths per cent. of the seed.

II. A small quantity of proteose, the reactions and composition of which could not be definitely ascertained.

III. Edestin, a globulin which is the same as that found in the wheat and rye kernels and in a large number of other seeds. Its composition is approximately shown by the figures given below. Owing to the small amount of this body and the difficulty in preparing it, no perfectly pure preparations were obtained.

Carbon	50.88
Hydrogen	6.65
Nitrogen	18.10
Sulphur } Oxygen }	24.37
	100.00

This is the proteid commonly known as vegetable vitellin. It is precipitated from saline solutions by dilution and by dialysis, is not coagulated by heating below 90°, and above that temperature only partially. It is not precipitated by saturating its solution with sodium chloride, but is thrown down from saline solutions by adding acid.

IV. Hordein, a proteid insoluble in saline solutions, very slightly soluble in pure water, and extremely soluble in alcohol of about seventy-five per cent. This is the barley proteid described by Ritthausen as mucedin. It has almost the same physical and chemical properties as gliadin obtained from wheat and rye kernels but a different composition.

Carbon	54.29
Hydrogen	6.80
Nitrogen	17.21
Sulphur	0.83
Oxygen	20.87
	100.00

About four per cent. of the seed consists of this substance.

V. After extracting the barley flour with salt solution and with alcohol the residue still contained forty-two per cent. of the total nitrogen, corresponding to proteid-matter equal to about four and five-tenths per cent. of the flour. It was not possible to extract more than a very small amount of this residual pro-

teid with dilute potash water, as the treatment for removal of the other proteids rendered it insoluble, if it were not so already.

VI. The barley flour contained 1.83 per cent. of nitrogen, and if it be assumed that this all belonged to proteid-matter with seventeen per cent. of nitrogen, the flour would contain 10.75 per cent. of proteids. The barley accordingly contained about four and a half per cent. of insoluble proteid, four per cent. of hordein soluble in dilute alcohol, three-tenths per cent. albumin, and 1.95 per cent. of globulin and proteose.

THE DETERMINATION OF NITROGEN IN FERTILIZERS CONTAINING NITRATES.[1]

By H. C. Sherman.

Received April 13, 1895.

As soon as the accuracy of the Kjeldahl method for the determination of nitrogen was generally recognized, attention was turned toward the discovery of some simple modification by which it could be made applicable in the presence of nitrates.

Asboth (*Chem. Centrbl., 1886*) recommended the simple addition of benzoic acid to the decomposing mixture. It was soon found that this method was not sufficient.

The following year, two methods were brought before the Association of Official Agricultural Chemists, one by Mr. Scovell, the other by Mr. Farrington. The principal difference consisted in the use of salicylic acid with the sulphuric acid to fix the nitrogen oxides by the former, while phenol was used for the same purpose by the latter. Both used zinc dust as the reducing agent. The Scovell method was adopted and remains practically unchanged.

In 1890, the Association sanctioned the use of zinc sulphide as a reducing agent. In case of its use the acid mixture was to contain one gram of salicylic acid instead of two. The use of zinc dust with two grams salicylic acid was retained.

In 1892, sodium thiosulphate, which had been used for reducing nitrates in the Ruffle method, was adopted as a third reducing agent, and it was directed that five grams of the crystalized salt should be added "direct."

[1] Read before the Washington Section.

In 1893, the use of zinc sulphide was dropped, (because this reagent was likely to contain nitrogen) and a modification of the Gunning method was adopted. In the latter, five grams of thiosulphate and one gram of salicylic acid were used with the same amount of potassium sulphate as in the plain method (ten grams). It was claimed that that all the reagents could be added with the substance, but further trials disproved this, and in 1894 the requirement of first mixing the substance with the acid mixture was made practically the same as in the modified Kjeldahl.

It has been the experience of the writer, and the amount of work which has been done by the Association, indicates that it is the same with others, that the determination of nitrogen in fertilizers containing nitrates is attended with greater difficulty than in those free from nitrogen in this form. In the hope of discovering whether this is due to any considerable extent to the official methods, and, if so, the reasons therefor, the following experiments were undertaken.

A set of four samples was first prepared, composed of the following materials:

No. 1, sodium nitrate, ammonium sulphate, potassium chloride, acid phosphate.

No. 2, sodium nitrate, bone phosphate, dried blood, ammonite, marl filler.

No. 3, sodium nitrate, tobacco stems, cottonseed-meal, castor pomace.

No. 4, sodium nitrate, dried fish, natural guano.

In each case all the materials, except the nitrate, were first mixed, ground to pass through a five-tenths mm. sieve, and air-dried. Nos. 1, 2, and 3 were then mixed again, and the percentage of nitrogen carefully determined by both the Kjeldahl and Gunning methods. The guano used in preparing No. 4 contained a small amount of nitric nitrogen, and could not be determined in this manner.

An air-dried sample of sodium nitrate was then ground to pass through the same sieve, and its nitrogen content determined by the silica fusion method. This sample was then carefully mixed with those above described in such proportions as to give to each the desired percentage of nitrogen. Nos. 1, 2, and 3 were cal-

culated to contain ten per cent., eight and one-half per cent., and eight and one-half per cent. respectively. No. 4 was expected to show about eight per cent. These percentages are as high as are likely to be found in ordinary mixed fertilizers.

The materials employed represent all the general classes of ingredients commonly used in this section, and since no one of them composed less than fifteen per cent. of the mixture in which it occurred, any effect which it might tend to produce would be almost sure to be noticeable in the result.

The results on these mixtures by the official methods are given in Table I.

TABLE I. PER CENT NITROGEN FOUND IN KNOWN MIXTURES.

No.	Calculated.	Modified Kjeldahl Zinc dust.	Modified Gunning.
1	10.00	9.93	9.80
2	8.50	8.51	8.50
3	8.50	8.48	8.50
4	...	8.12	8.08

Except in the case of No. 1, the figures given are the averages of two (and only two) determinations. The greatest difference between duplicates was 0.08 per cent.; the average difference 0.03 per cent.

Four determinations were made by each method on No. 1. These are given below.

The official methods as given on page 347 (Bul. 43, U. S. Dept. of Agr., Division of Chemistry) were followed closely with the following additional precautions.

1. In working the modified Kjeldahl method, the zinc dust was added through a funnel tube, very slowly, and with constant shaking. About two minutes is required to add the zinc dust in this way. After the first boiling, the flasks were allowed to cool somewhat before the mercuric oxide was added.

2. In the modified Gunning method, the boiling was continued about thirty minutes after the contents of the flask had become "nearly colorless."

To test these points determinations were made on Nos. 2, 3, and 4 without the precautions noted, but in every other way as above. The average results, together with those given above, are shown in Table II.

TABLE II. SHOWING EFFECT OF PRECAUTIONS NOTED ABOVE.

		Modified Kjeldahl:		Modified Gunning:	
			Zinc added in three to five portions and HgO at boiling heat.		Boiling stopped when nearly colorless.
No.	Calculated.	As above.		As above.	
2	8.50	8.51	8.47	8.50	8.55
3	8.50	8.48	8.46	8.50	8.36
4	8.10[1]	8.12	8.05	8.08	7.95
Av.	8.37	8.37	8.33	8.36	8.22

It is noticeable that the duplicates agreed about as closely as when the precautions were taken, but the results were in every case too low. The average discrepancy was, in the Kjeldahl, 0.04 per cent.; in the Gunning, 0.14 per cent. It would seem, therefore, that both of these precautions are advisable, and the second absolutely necessary, at least when working with high percentages.

Table III shows the results obtained on No. 1 by the modified Kjeldahl and Gunning methods, and by Winton's modification of the latter.

TABLE III. RESULTS ON SAMPLE NO. 1.

Calculated.	Modified Kjeldahl.	Modified Gunning.	Winton's Modification.
10.00	9.93	9.86	10.03
....	9.98	9.72	9.97
....	9.97	9.83	9.99
....	9.84	9.80	10.02
Average	9.93	9.80	10.00

The results by Winton's method are highly satisfactory; those by the Kjeldahl hardly so when compared with the other samples, while the Gunning gives results which are entirely too low to be called good.

Winton's modification of the Gunning-Kjeldahl method is essentially as follows: The substance is treated with the usual acid mixture and allowed to stand two hours, with frequent shaking. Two grams of zinc dust are then added and the first heating performed as in the Kjeldahl. Potassium sulphate is then added and the operation finished as in the Gunning method. It

[1] Average by both methods, see above.

is, therefore, a combination of the two with the improvement of the longer digestion in the acid mixture.

To return to the results on sample No. 1, since all the mixtures contain more or less phosphoric acid, the only substances peculiar to this sample are ammonium sulphate and potassium chloride. Since ammonium sulphate is formed in the process and is the final form of all nitrogen present, its presence in the sample could hardly account for the discrepancy, which, therefore, appears to be due to the chloride.

In looking over the record of the Association of Official Agricultural Chemists, we find that the modified Kjeldahl method has been tested by the Association in the year of its adoption and, with one exception, every year since on from one to five samples. Only four of these have contained chlorides, and only one in any considerable quantity. The modified Gunning has been tested by the Association on only one sample containing chlorides. These samples with the approximate percentages of chlorine, total nitrogen, and nitric nitrogen, and the variation in results reported, expressed in percentage of total nitrogen present, are shown in Table IV. All results which are so far from the average as to indicate accident are omitted, according to the custom followed by the reporters of the Association in averaging their results.

TABLE IV. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. SAMPLES CONTAINING CHLORIDES.

Sample	Method	Chlorine, per cent.	Total Nitrogen, per cent.	Nitric Nitrogen, per cent.	Variation, per cent.
No. 4, 1888	Modified Kjeldahl	5	3.16	1.64	33.4
No. 1, 1889	" "	1.5	15.91	15.91	3.0
No. 3, 1889	" "	2.5	3.55	1.48	14.1
No. 2, 1893	" "	1.5	5.77	3.47	8.8
No. 2, 1893	Modified Gunning	1.5	5.77	3.47	7.5

To further test this question, determinations were made, in duplicate, on samples Nos. 2, 3, and 4, with one-half gram of potassium chloride added. Table V shows the average results with and without chlorides, the methods being carried out in exactly the same way as before.

TABLE V. PER CENT NITROGEN FOUND WITH AND WITHOUT CHLORIDES.

		Modified Kjeldahl.		Modified Gunning.	
No.	Calculated.	Without KCl.	With KCl.	Without KCl.	With KCl.
2	8.50	8.51	8.37	8.50	8.35
3	8.50	8.48	8.40	8.50	8.25
4	8.10	8.12	8.04	8.08	7.92
Average	8.37	8.37	8.27	8.36	8.17

A portion of the sodium nitrate used in preparing these mixtures was now taken. It had shown by the silica fusion method 16.41 per cent. nitrogen. The modified Kjeldahl showed 16.39 per cent and 16.38 per cent.

Portions of one-half gram were taken for each determination, and mixed with the same amount of potassium chloride. The digestion was carried out in the usual way.

The results were:

Modified Kjeldahl.	Modified Gunning.
16.32	15.82
16.09	15.68
15.96	15.83
15.97	15.46
16.23	16.02[1]
15.95	15.99[1]
16.07	15.86[1]
16.13	

The Winton modification was then tried and care taken to warm gently for some time after adding zinc dust before raising the heat, which was done gradually.

Results were:

	16.27
	16.30
	16.30
	16.34
Average	16.30

Indicating that the greatest care in the reduction process will not entirely prevent loss.

To ascertain more definitely at what stage in the operation the loss occurs, mixtures of one gram each sodium nitrate and potassium chloride were treated as in an analysis, and the gases escaping from the flask were made to pass through a bulb-tube

[1] Two grams salicylic acid used.

containing potassium hydroxide. The nitrates and nitrites thus recovered were converted into ammonia and estimated by means of Nessler's reagent, using for comparison a solution of ammonium chloride containing 0.0001 gram nitrogen in each cc. The operation was divided into four stages: (a) addition of sulphuric salicylic acid mixture; (b) addition of reducing agent; (c) gentle heating till frothing ceased; (d) brisk boiling for a few minutes. After evolution of gas had ceased in the first and second stages, and after removal of the flame in the fourth, a glass tube was inserted through the stopper reaching nearly to the surface of the liquid, the bulb-tube attached to an aspirator, and the gases contained in the flask thus drawn through the alkali. The following table (VI) shows the results obtained, expressed in terms of per cent. nitrogen on the basis of one gram substance:

TABLE VI

		Nitrogen Recovered.					
Reducing Agent used.	Temperature.	a.	b.	c.	d,	Total.	b, c, and d.
Zinc dust	20°	0.023	0.006	0.026	0.008	0.063	0.040
" "	24°	0.027	0.005	0.034	0.013	0.079	0.052
$Na_2S_2O_3$ in presence of K_2SO_4	22°	0.090	0.027	0.061	0.017	0.195	0.105
$Na_2S_2O_3$ in absence of K_2SO_4.....	20°	0.090	0.027	0.035	0.013	0.165	0.075
Zinc dust[1]	27°	0.039	0.001	0.006	0.011	0.057	0.018

Where zinc dust was used the acid mixture contained two grams of salicylic acid; where thiosulphate was used, one.

The results indicate: 1. That the greatest losses occur on the addition of the acid mixture and on the first application of heat. The former is thought to be due to the liberation of hydrochloric acid in direct contact with the nitrate before the mass has become thoroughly wetted by the sulphuric salicylic acid mixture.

2. The total loss exclusive of the first stage is greater with thiosulphate than with zinc dust, and appears to be greater when potassium sulphate is added with the thiosulphate than when the latter is added alone. By exercising care in the addition of the reducing agent and the application of heat, the loss in the last three stages is reduced to a very small amount.

[1] Some precautions taken as in working Winton's modification on mixture of nitrate and chloride, see above.

3. At a given temperature, the loss on addition of acid is greater where the mixture containing less salicylic acid is used.

4. Using the same quantity of salicylic acid, the loss on addition of the acid mixture appears to increase with the temperature.

5. The total amount of nitrogen recovered being less than the average discrepancy showed by analysis under similar conditions, it appears probable that there may be some loss later on in the process.

These facts explain why the Kjeldahl gave better results on a mixture of nitrate and chloride than did the Gunning; while the Winton gave better than either.

In this connection the heat generated on the addition of the reducing agent is of interest. The average of seven determinations each on zinc dust and thiosulphate, both added in the usual way, showed, for the former, an increase of temperature of 21°; for the latter, of 40°.

In the opinion of the writer, the prolonged digestion of the Winton method is useful, in the presence of chlorides, not only in securing complete solution of the nitrate, but also in allowing the contents of the flask to cool (for the heat generated by the action of the acid mixture on the chlorides is considerable) and to absorb a slight amount of moisture from the air, thus rendering the action less violent when zinc dust is added.

Mixtures of one-half gram each sodium nitrate and potassium chloride, treated with acid mixture cooled down to 8°, and digested as in the Winton method before addition of zinc dust, showed by the modified Kjeldahl method 16.34 per cent. and 16.32 per cent., or 99.6 per cent. of the amount found in the absence of chlorides.

Determinations by the modified Gunning on the same mixtures, in which the acid mixture was cooled to from 8° to 12°, the thiosulphate added slowly and with constant shaking and cooling of the flask, and the boiling continued some time after the liquid had become colorless, showed 16.02 per cent., 15.88 per cent., 16.16 per cent., and 15.99 per cent.; average, 16.01 per cent., or only 97.8 per cent. of the amount found when chlorides were not present.

Determinations on the same sample of pure nitrate alone by the modified Gunning method, carried out in slightly different ways, gave the following results:

As usually carried out with mixed fertilizers, 16.16 per cent. and 16.13 per cent.

Thiosulphate added first and heated before adding potassium sulphate, 16.16 per cent. and 16.24 per cent.

Thiosulphate added slowly with shaking and cooling, but digestion stopped as soon as liquid became colorless, 16.10 per cent.

Thiosulphate added as above, digestion continued one hour after colorless, 16.31 per cent. and 16.32 per cent.

As above, permanganate used, 16.37 per cent.

Modified Kjeldahl, using thiosulphate (five grams added direct), showed 16.37 per cent. and 16.36 per cent.

It may be well to state now that all the results given in this paper are corrected for reagents. At first a blank was run with every five determinations. After three or four such blanks had been made for each method and found to agree closely, their average was taken and applied to every result obtained by that method. Whenever it was necessary to change any of the reagents, another blank was run.

The results here given would *seem* to warrant the following conclusions.

1. For ordinary fertilizers containing little or no chlorides, the official methods are perfectly reliable if the directions are followed closely and the digestion in the modified Gunning is continued for at least a short time after the liquid has become practically colorless. The discrepancies which sometimes occur under these circumstances are believed to be due to faulty preparation of the sample.

2. In working with samples containing considerable amounts of chlorides, it is advisable to use the modified Kjeldahl (zinc dust) method and to cool the acid mixture before adding it to the substance. It appears advisable also to digest for some time at ordinary temperature before adding zinc dust. No way has been found by which equally accurate results can be obtained by the modified Gunning method in the presence of large amounts of chlorides, together with high percentages of nitric nitrogen.

3. When determining high percentages of nitric nitrogen by the modified Gunning method, it is necessary either to continue the boiling for some time after the contents of the flask have become colorless, or to use permanganate to complete the action.

MARYLAND AGRICULTURAL COLLECE,
COLLEGE PARK, MD.,
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ON CONDENSATION; AND ESPECIALLY ON THE CONDENSATION OF NITRIC ACID.[1]

BY EDWARD HART.

Received January 7, 1895.

THE ideal condenser, economically considered, is the one simplest in construction, most accessible for repairs or other purposes, and which, with a given efficiency, requires the least cooling liquid. The old-fashioned worm is certainly far removed from this ideal. The Liebig's condenser is a nearer approach. If the space between the inside and outside tube in Liebig's apparatus is made narrow enough it is possible to effect complete condensation in a relatively short tube, and to raise the cooling liquid to boiling temperature. At first sight it would seem that this gives a maximum efficiency; but it does not. If the water used as cooling liquid has, at the start, a temperature of 0°, and, as it issues from the condenser, a temperature of 100°, the heat absorbed by a given weight of water is approximately 100 units. If, however, the cooling liquid can also be made to evaporate, the heat absorbed is much larger in amount, and is equal to 100 units plus the amount required to evaporate it (526 units). This makes in all 626 units, or an efficiency six times as great. In the Liebig's condenser, also, the liquid condensed is cold or nearly so. In many cases this is not necessary and then an additional loss is sustained.

In the apparatus which I shall describe a very brief consideration will show that the maximum of efficiency may be attained. For, first, the cooling water is evaporated; second, the condensed liquid is boiling hot.

This condenser I have used in several modified forms adapted

[1] A paper with this title was read at the World's Congress of Chemists, Chicago, August 26, 1893. The present paper has been revised to accord with more recent experience and practice.

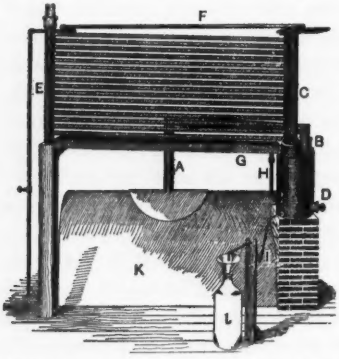
to various special purposes, among others, to the cooling of ammonia gas and the condensation of nitric acid.

In its simplest form, as used for preparing distilled water for example, the apparatus consists of a pipe with return bands placed one above the other, so that the vapor passes through the pipe in an upward direction, first right then left then right again, and so on, the bends rising one directly over another.[1] This pipe should be so large in diameter that the liquid may flow down in the lower part of the tube while the vapor is passing upward above it. For the same reason each bend of the pipe should have a slight rise so that the water may run down more rapidly. At the lower end the pipe should be enlarged and provided with an inverted siphon to act as a trap and carry off the condensed water. If, now, steam be passed up the pipe and water showered over the topmost bend, the water will, as it trickles down, become heated and evaporate. It is clear that by properly regulating the flow of steam and of water, we may secure complete condensation of the former and complete evaporation of the latter; at the same time the condensed water as it passes from the trap will have the boiling temperature. The cooling effect, if the apparatus is placed in the open air, is greater even than theory would predict for we have the additional cooling effect of the air. I have used this apparatus also for the separation of water vapor from ammonia gas, and for cooling the latter previous to condensing it. The conditions here are much the same as in the apparatus for distilled water. It is necessary to keep the condensed water at boiling heat to prevent reabsorption of ammonia, and in practice we find that very little ammonia is contained in this condensed water. The inclined tube acts besides as a very effective washer for the gas, completely removing any impurities mechanically carried over from the still. If it is desired to cool the condensed liquid, this is best done in a smaller apparatus of the same sort in which the current of liquid passes in an upward direction.

In the condensation of nitric acid the substances which can be used for the condenser are glass and stoneware, and it is therefore best to modify the apparatus somewhat, for the sake of sim-

[1] I have previously described a form of this apparatus which may be used for fractional distillation. See Am. Chem. J., 6, 178.

plicity and for decreasing the pressure in the pipes, which causes loss and annoyance by leakage through joints, and pinholes in the stoneware. With this in view the stream of vapor has been subdivided by passing it through a number of glass tubes with slight fall sufficient to allow the condensed liquid to flow back into the receiver. In the apparatus shown in the figure, the



upright tubes at either side are made of stoneware, the connecting tubes are of thin glass. The pipe A, made of stoneware, carries the nitric acid vapors from the retort into the pot B provided with a stopper, D, which is taken out if frothing should occur and allows the froth to escape without danger of filling the condenser. The vapors pass up into C and are distributed through the glass tubes luted into it. The condensed acid runs back and is discharged through the glass trap I into the container J.

The use of the glass tube is of great advantage since the color and amount of acid can be seen throughout the distillation and the firing regulated accordingly. From the pot the vapors ascend into the stoneware pipe and pass through the nearly horizontal glass pipes let into it into another similar stoneware tube on the left, from which the chlorine and lower oxides of nitrogen escape to the chimney or tower. These tubes are slightly inclined, and the acid condensing runs back into the pot. In running back it becomes very hot by contact with the vapors coming over and is deprived of the oxides of nitrogen. Condensation is effected by running water over the glass tubes from the perforated pipe above.

This apparatus is, to a certain degree, self-regulating. It never happens that the tubes condense the gas in equal amount. One of them is thinner or a little wider, and as condensation is more rapid the flow of gas into the tube is more rapid. But, in

any event, the pressure is equal in all the tubes, and only when the distillation is hurried too much will any uncondensed vapor pass through. There are fifteen tubes to each condenser about an inch in diameter and six feet long.

Two of these condensers have been in use for nearly two years at the works of Baker and Adamson, Easton, Pa., and the system has, therefore, had a thorough test. The retorts used here are cylindrical, as shown in the cut, and are made entirely of cast iron with iron heads. The niter-cake is drawn while fluid. These retorts each hold a charge of 1,000 pounds sodium nitrate. They are charged at 7 A. M. and the operation finished at 3. P M., a *total of eight hours*. The best practice by the Griesheim system is, ordinarily, a charge of eight cwt. in twenty-four hours; under favorable conditions, and with a good fireman, sixteen hours are needed.

The floor-space required in this apparatus is reduced to a minimum. The condensers are, as shown in the cut, placed over and above one side of the brick arch which covers the cylindrical retort, so that absolutely no additional floor-space is required, all that is needed being sufficient room to pass conveniently between the retorts.

One man can run several retorts. All the assistance needed is that of a helper in discharging the retorts and in emptying the salt cake from the pans. These operations will require, perhaps, half an hour each.

In another place I have already (*J. Anal. Appl. Chem.*, **5**, 382) pointed out the advantages of giving a cylindrical form to the retort, which requires less floor-space, less cost for masonry, and is less expensive in coal consumption. The form I have used is very much superior to, and quite different from, any of the patterns shown by Guttmann (*J. Soc. Chem. Ind.*, **12**, 203). In brief, this new form of condenser has the following good points:

1. It gives great efficiency with small first cost.
2. It requires but little water.
3. It requires but little floor-space.
4. It reduces the pressure and so reduces leakage.
5. It is easily and cheaply repaired.

SOME POINTS IN THE DISTILLATION OF NITRIC ACID.[1]

By Edward Hart.

Received January 7, 1895.

IN a previous paper I described a tube condenser for use, among other things, in the condensation of nitric acid. Further experience with this condenser has enabled us to obtain still better results. We can now obtain a distillate very low in nitrogen peroxide. The specific gravities of the distillate are about as follows:

84	pounds.	1st	distillate.....	Sp. gr.,	1.527
83	"	2nd	"	"	1.526
83	"	3rd	"	"	1.523
82	"	4th	"	"	1.512
77	"	5th	"	"	1.504
77	"	6th	"	"	1.493
74	"	7th	"	"	1.487
74	"	8th	"	"	1.485
47	"	9th	"	"	1.474
47	"	10th	"	"	1.448
57	"	11th	"	"	1.300
785	"				

The amount of fuel necessary is surprisingly low if proper care is taken. For the distillation of 1,000 pounds nitrate, we use regularly but 150 pounds of pea anthracite coal, working day turn only; this is, no doubt, largely due to the short time within which the distillation has been brought by the use of this condenser, the distillation proper occupying but six hours, and the entire time, including charging and discharging, eight hours. During the night the retort and masonry, of course, cool off. I have no doubt that by running two shifts—day and night—the coal necessary could be brought within 125 pounds for the same weight of nitrate.

Source of the Nitrogen Peroxide Produced.—The contrast in color between nitric acid produced on the small scale in glass, and that made on the large scale in iron retorts, is very noticeable and I have been at some pains to look into the cause, since this formation often represents a dead loss to the manufacturer. I shall later on call attention to a period in the ordinary distillation during which, with no increase in the firing, the acid

[1] Read at the Boston Meeting, Dec. 27, 1894.

comes over very rapidly. It has often been noticed that during this stage, the acid is unusually white. I attribute this to the rapidity with which the gas passes from the retort, and consequent decrease in decomposition caused by the radiated heat. The same thing is noticed by distilling in glass. Certainly, therefore, part of the nitrogen peroxide is due to too long heating of the vapor, and the importance of an efficient condenser and a rapid distillation is evident.

The effect of concentration of the vitriol on the color is very evident. The ease with which concentrated nitric acid is decomposed is well-known and, as might be expected, the strong acid made from distilled vitriol and dry nitrate shows much stronger color than that made from the less concentrated materials. In glass, heating over a Bunsen, such acid may be obtained without difficulty of only a pale straw color, but in the ordinary iron retort the crude aqua fortis will frequently contain as much as three per cent. nitrgen peroxide.

It is the common opinion among acid makers that part of this color, perhaps a large part, is due to action of the acid on the iron. In most cases this is no doubt true, as the retort, as ordinarily set, is but imperfectly heated at the ends. In the retorts which I have been using, however, the retorts are *entirely* surrounded with the fire gases. It is quite possible, however, that even here the iron is notably attacked. Part of the color, no doubt, arises from impurity of the materials—chlorine, organic material, and iron in solution principally—but I suspect that this is responsible for only a part of the trouble. A gentleman who has for years carried on the distillation of nitric acid on the large scale, recently informed me that he had distilled fused nitrate and white vitriol in iron with no perceptible diminution of the color in the product.

As stated in the books, the only reactions occurring are

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3, \text{ or}$$
$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

In practice only the first reaction is usually employed, especially where, as in acid for mixed acids, to be used for nitroglycerol, the product must be as concentrated as possible. In this

connection, however, one point I think should be noted that seems to have escaped attention, that is, that with weak vitriol the water is largely retained by the cake until the last stage of the operation, and greatly assists the decomposition giving a fair acid and a cake which is practically infusible. If, however, strong vitriol is used, the decomposition is incomplete and the acid exceedingly red.

The Frothing.—This matter of frothing is one that frequently gives great trouble to the nitric acid distiller, especially where weak acid and wet nitrate are used. The frothing begins in such cases after about seven-elevenths of the acid has distilled over.

This is easily demonstrated by conducting a distillation in glass with acid of 1.80 sp. gr., or less. The trouble becomes then plainly apparent, and is evidently due to the decomposition of the $NaHSO_4$ at first produced into $Na_2S_2O_7$ and water: $2NaHSO_4 = Na_2S_2O_7 + H_2O$. That this is the reason may easily be demonstrated by heating in another similar retort a mixture of dry sodium sulphate and sulphuric acid. We then have $NaHSO_4$ formed, and on continuing the heat the same frothing is noticed, although the distillate is, of course, entirely free from nitric acid. Frothing over is prevented by giving sufficient capacity to the retort, and by care and skill in firing. Neither alone is sufficient to prevent it.

Rate of Distillation.—One of the most remarkable things in the distillation, especially noticeable in glass and with pure dry materials, is the variation in the rate of distillation and the almost explosive evolution of acid, which takes place, for a short period, after about three-tenths of the acid has distilled over. For example: In distilling in glass 200 grams sodium nitrate and 235 grams distilled sulphuric acid, the proportions required by the equation $NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$, the following results were obtained. It should be understood that the Bunsen, over which the operation was conducted, was allowed to remain untouched, except where noted, and that the apparatus was shielded from air currents. The thermometer bulb was shielded from radiation by placing it within a porcelain crucible in the retort.

Time.	Time interval.	Temperature.	Temperature interval.	Acid distilled.	Remarks.
1 : 46 : 40	.....	108°	...	..	Distillation begun.
2 : 48 : 23	1 : 43	110°	2°	5	
2 : 50 : 20	1 : 57	113°	3°	10	
2 : 52 : 30	2 : 10	117°	4°	15	
2 : 55 : 15	2 : 45	124°	7°	20	
2 : 59 : 00	3 : 50	128°	4°	25	
3 : 02 : 00	3 : 00	133°	5°	30	Froth rises.
3 : 02 : 55	0 : 55	125°	—8°	35	Froth very high.
3 : 03 : 30	0 : 35	125°	0°	40	Froth sinking.
3 : 04 : 00	0 : 30	125°	0°	45	No froth
3 : 04 : 45	0 : 45	126°	1°	50	No froth.
3 : 17 : 40	12 : 55	135°	9°	55	Mushy mass fusing to clear liquid below.
3 : 23 : 30	5 : 40	148°	13°	60	Half fused.
3 : 38 : 30	.....	157°	9°	65	Three-fourths fused.
3 : 45 : 20	.....	152°	—5°	70	Piece of cake dropped into fused mass, lowering temperature.
3 : 52 . 00	.....	158°	Acid not running, clear fusion, lamp turned up.		
3 : 58 : 30	.....	170°	12°	75	No froth.
4 : 03 : 00	.....	178°	8°	80	No froth.
4 : 04 : 45	.....	180°	Lamp turned still higher.		
4 : 06 : 00	.....	194°	14°	85	Slight froth.
4 : 08 : 15	.....	200°	6°	90	Half-inch froth.
4 : 12 : 20	.....	220°	20°	20	Retort full of froth during this interval.
4 : 16 : 00	.....	246°	26	96	Froth gone, lamp turned out.

The drop of the temperature at 133° is, I think, unmistakable, and reminds one of the rise of temperature produced in the crystallization of a supersaturated solution. There we have the change from the fluid to the solid condition—here from the solid to the fluid. This explosive evolution is noticeable also in distilling in iron on the large scale and, perhaps, explains in part the difficulty nitric acid makers have hitherto had in properly condensing their product. By proper firing, and with a properly set retort, this difficulty is lessened.

To decompose strong nitric acid by heat or by its action on iron, and then to drive off the nitrogen peroxide with great pains and loss, is evidently a clumsy and probably unnecessary operation. I shall, therefore, make a determined effort to so arrange the retort that this will be in future unnecessary. There would seem to be no insuperable obstacle in the way of so conducting the distillation that even the first distillate would be of a pale straw color, like that made in glass, and quite fit for the manufacture of dynamite and other nitro compounds with no purification whatever.

The use of nitro compounds has, of late years, become so large that a rational method of conducting the process of nitric acid distillation is imperatively called for.

Berthelot has shown that strong nitric acid is completely decomposed at about 360° into nitrogen peroxide, oxygen, and water. It is certain that with the retorts entirely surrounded by fire gases the temperature of the upper part of the retort exceeds 100°. It is not surprising, therefore, that the first distillate should show a dark red color. A recent distillation in glass, with pieces of cast iron immersed in the mixture of acid and nitrate, gave no additional color to the first distillate.

NEW BOOKS.

COD-LIVER OIL AND CHEMISTRY. BY F. PECKEL MÖLLER, PH.D. London: Peter Möller. New York: Wm. H. Schieffelin & Co. Printed for private distribution.

This book is really two books in one. The first part treats of cod-liver oil, the methods of catching the fish, the preparation of the oil, and an account of its constituents. We learn that cod-liver oil was originally made from fresh cod-livers by the steam process, by Peter Möller, in 1853. The oil so prepared was a great improvement over the older product prepared by the putrefaction of the livers. It still, however, caused disagreeable after-effects when exhibited, and to remedy this an investigation was undertaken by P. M. Hyerdahl, presumably in the employ of Peter Möller. Mr. Hyerdahl finds that the disagreeable after-effects are caused by the presence of hydroxy acids in the oil, and that these may be excluded by rendering the livers in an atmosphere of carbon dioxide. This process is now carried out by Peter Möller, therefore buy your cod-liver oil of this firm. The deduction is not so stated in the book, which is well written and gives a very readable account of the subject, but the advertising purpose is obvious.

It is a pity that Mr. Hyerdahl's work was not made known through the regular channels—the *Berichte* for example. Chemists will be apt to look with suspicion upon statements so obviously interested.

The second part of the book is a treatise on organic chemistry of an original sort. The author has used the Daltonian symbols in modified form, and the result is, as might have been expected, that the poor devil of a printer has had a hard time of it. So long as printing is done as at present, authors should beware of using new characters; by so doing they not only increase the already difficult task of the printer but really put themselves at his mercy. If only one printer have the character he must be allowed to do the printing of course. While such symbols have certain advantages, their disadvantages seem greater. Only a few people seem to be able to remember that, after all, our symbols represent only very imperfect knowledge, and that they are only tentative. A chemist can, therefore, read this treatise with interest and profit; it can scarcely be considered a good book for beginners, but it was probably not intended for beginners.

EDWARD HART.

THE INCREASE IN WEIGHT OF TIN AND LEAD ON CALCINATION. BY JEAN REY, 1630. Alembic Club Reprints, No. 11. 54 pp. Edinburgh: William F. Clay, 1894.

Rey is one of the less well-known investigators of the seventeenth century. He is properly to be classed with Hooke, Mayow, and Boyle, or the Oxford School of Chemists, as Thorpe has fitly called them, in their work upon the increase of weight of the metals when calcined, and the part played by the air in these processes. That which Thorpe has so well done for the others is now done for Rey in this little book. The quaintness of the original is well preserved in the translation, and the book is very valuable as giving an insight into the wisdom and the childishness of the times. His self-applause in the triumphant summing up of the evidence in support of his theory, that the air played an important part in the phenomena observed, is delicious.

The Alembic Club is doing a most valuable work for the science in the republication of these early essays. They are interesting and helpful to the earnest student and should have a wide circulation.

F. P. VENABLE.

OBITUARY.

PROFESSOR MARK POWERS.

Professor Mark Powers, a member of the American Chemical Society, died in Chicago, March 1st, of smallpox.

Professor Powers was born near Muncie, Ind., November 13th, 1864. In September, 1883, he entered the Freshman class of the University of Illinois, where, in time, he gave special attention to chemistry, then in charge of Professor Wm. McMurtrie. He was graduated from the University, with the highest honors of his class, in June, 1887. In September of the same year he came to Chicago to take the position of Assistant in the Chemical Laboratory of the School of Pharmacy of the Northwestern University. At the time of his death he was Assistant Professor of Chemistry in the same institution.

Professor Powers possessed unusual ability as an analyst and investigator, yet, on account of his many duties in the laboratories, he was able to publish only one scientific paper. This was a valuable contribution on "The Decomposition of Organic Matter in Water," and is found in the *Journal of Analytical Chemistry*, Vol. III. As a teacher his work was of the highest order, and it was in this direction, rather than in that of investigation, that he chose to make a reputation.

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